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THE SOLUBILITY OF PRECIPITATES IN THE PRESENCE OF COMMON IONS AND OTHER IONS[1)]

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The Effect of Chemical Factors, and the Effect of the Ionic Strength on the Stability of Precipitates

The solubility of precipitates is one of the most characteristic factors to be considered in the separation of the elements, and in the many methods of determining them. Solubility depends on different factors: concentration of the common ions, the acidity of the solution, the presence of complex-forming substances, the presence of non-aqueous solvents, and the temperature and ionic strength of the solution. Unfortunately during the last 20-30 years most of the work carried out has been done on the effect of the last factor. On the other hand far too little attention has been paid to the effect of chemical factors, it being sometimes assumed that experiments based on the principle of the solubility product have no scientific significance, as if this principle were only of empirical value which is often not justified experimentally.

The relation between solubility product Lp and activity product La was considered in 1943 by A. F. Kapustinsky [1] who also showed the connection of La and Lp with the thermodynamic expression for free energy. The chief defects of work based on the study of the action of strong electrolytes are the following. There is no exact physical picture of the relationship between ionic activity and the ionic strength of the solution. The equations of Debye, Huckel and others give better agreement between theory and practice, the more empirical coefficients they introduce into these equations. Further, chemical factors are often completely ignored. Thus the effect of excess common ions on the solubility of a precipitate is considered exclusively in the light of Debye and Huckel's theory. Meanwhile it is completely obvious that complexes are formed by interaction between certain compounds, as has been shown, e.g. between $PbCl_2$ and NaCl, AgI and KI (and with $AgNO_3$), and $PbSO_4$ with acetates, etc. Complex ions are also formed by the interaction of highly charged ions with precipitates, [e.g. Zr^{4+} with $Zr(C_2O_4)_2$ to form $ZrCr_2O_4^{2+}$, etc.], nevertheless, these reactions

1) Reported at the Conference on Classical Method of Chemical Analysis held in Moscow 14-17 November 1951.

and numerous other chemical reactions are not taken into consideration, the results being attributed to the effect of strong electrolytes.

Finally the effect of the ionic strength of solutions is comparatively small. Even for ionic concentrations where maximum deviation between the numerical values of the concentrations and ionic activity is observed, the change in solubilities is rather small. Thus, for the most common precipitates of the 2-2 valency type ($BaSO_4$, CaC_2O_4, etc.,) the following relationship can be established. The relation between La and Lp is expressed by the equation [1]:

$$Lp = \frac{La}{f^2},$$

where f is the activity coefficient. The neutralized activity coefficient for doubly charged ions for an ionic strength $\mu = 0.1$ amounts to $f = 0.25$ [2]. Thus for $\mu = 0.1$, the solubility product increases to the value given by

$$Lp = \frac{La}{f^2} = 16La,$$

i.e. to 16 times the solubility in the absence of other electrolytes. This calculation shows that for accurate experiments, it is essential to consider the effect of other electrolytes. The simplest method of doing this is to insure a constant ionic strength in any series of experiments; obviously, in this way Lp will be constant. Such conditions correspond very well with normal analytical conditions, since in order to dissolve the substances being examined (alloys, silicates, etc.), a considerable amount of acid, alkali, or other reagents is used. Precipitation therefore usually occurs in the presence of an appreciable, and sufficiently constant amount of other electrolytes. Thus the effect of the ionic strength can be easily eliminated, and be made constant, just as is usually done with the temperature, which is of no less importance than the ionic strength.

Consequently, there is no basis for assigning any exceptional importance to the non-chemical effect of other electrolytes. Even in the least favorable cases the effect can change the solubility only ten times. On the other hand, chemical factors (presence of common ions, pH of the solution, complex compound formation, etc.) can change the solubility by a factor of 10^{20} or more. There is not a single analytical method based on the effect of strong electrolytes; the majority of methods used for separating and estimating elements is based on the effect of different chemical factors. This practical criterion shows that in the study of the solubility of precipitates, chief attention should be given to the questions of the influence of common ions, the acidity of the solution, complex compound formation, and non-aqueous solvents.

The Chemical Effect of an Excess of Precipitant on the Solubility of the Precipitate

The best known and most often used consequence of the solubility product principle, is the lowering of the solubility of a precipitate on the addition of excess of a common ion, i.e. usually an excess of precipitant. However, this only holds in those cases where the formation of a precipitate BA is the only form of chemical reaction between a cation B and an anion A. In the majority of cases, however, the precipitate BA is only one of several forms of the product of reaction between the components. In all cases the use of excess precipitant decreases the concentration of the precipitated ion. Nevertheless, when this occurs, it is only in certain cases that the precipitated ion is transferred to

the solid phase of the same composition. In other cases, an excess of precipitant leads to the formation of new chemical compounds.

To one degree or another, all types of chemical interaction between precipitate and excess precipitant are known; precipitation reactions, i.e. the formation of other precipitates (besides BA), acid-base reactions, oxidation-reduction reactions, and complex compound formation.

An excess of precipitant can lead to a change in the composition of the precipitate, i.e. to the formation of a new solid phase. Thus precipitates of phosphates can be formed, the composition of which vary with the amount of precipitant (e.g. $CaHPO_4$ and $Ca_3(PO_4)_2$,etc. A number of characteristic cases of the formation of solid phases of different chemical composition for different amounts of excess precipitant has been studied by I.V.Tananaev and coworkers [3] for the case of metallic ferrocyanides.

Interactions of an acid-base character are also known. Thus, in certain cases, in the presence of excess metal cations, basic salts are formed. Excess of precipitant – multibasic acids – at low concentrations leads to a decrease in the solubility of the precipitate, while at high concentrations it dissolves the precipitate with the formation of acid salts (e.g., the formation of hydrocarbonates, hydrosulfides, etc.)

Nevertheless, of all the possible forms of chemical reactions between precipitate and excess precipitant, the most important is that of complex compound formation. It is well known that a large number of compounds, despite their low solubilities, can not be used analytically as precipitates, owing to their solubility in excess precipitant. Such, e.g., are the iodides of bismuth and mercury, the oxalates of copper, bivalent iron, and zirconium and the majority of metallic cyanides, etc. In the precipitation of many precipitates, it is necessary to insure conditions, such that the concentration of excess precipitant is not very high. Thus, e.g. $Al(OH)_3$ can be precipitated by alkali hydroxides just as well as by ammonium hydroxide, but excess alkali hydroxide dissolves the precipitate with the formation of aluminates. In the precipitation of silver halides, a large excess of precipitant also leads to an increase in the solubility of the precipitate, etc.

Complex compound formation between excess precipitant and precipitate is one of the chief handicaps in the application of precipitates in analysis. Complex compound formation can be used in some cases for dissolving precipitates; unfortunately, although these reactions are very well known, they have been little studied.

Cases of increased solubility of the precipitate owing to the effect of excess anions are more common; in such cases complex anions are formed which are saturated (or near saturated) in the coordination sense. Nevertheless, detailed study of complex compound formation by a number of investigators in recent years has shown that such reactions proceed stepwise. In the chemistry of complex compounds the best known compounds are coordinately saturated complexes. However, those forces which lead to the formation of coordinately saturated complexes, in other conditions lead to the formation of stable,although coordinately unsaturated, complexes. If for any central ion B and a coordinated ion (usually an anion) A, a coordinately saturated compound BA_n is known, then a detailed investigation always shows that a whole series of coordinately saturated[1])

[1]) The central ion of these complexes may be coordinately saturated by combining with solvent molecules. The term "coordinately saturated" is used here in its usual sense for denoting compounds in which the central atom B is linked with an incomplete number of the coordinated ions A.

complexes exists in solution, which are related stepwise.

If one of the members of this series of complexes $\underline{BA}_m$, where $\underline{m}$ is less than $\underline{n}$, has a low solubility, then the properties of such a precipitate will have specific characteristics. By the addition of excess of a common ion $\underline{A}$, the solubility of the precipitate will increase as the result of the formation of complexes such as $\underline{BA}_{m+1}$, $\underline{BA}_{m+2}$ ... $\underline{BA}_n$. In addition, in consequence of what has been noted above, it should be expected that this precipitate will dissolve also in the presence of excess cations forming complexes of the series $\underline{BA}_{m-1}$, $\underline{BA}_{m-2}$, etc. Experiment shows that this actually occurs. Precipitates which dissolve in excess of their own (common) anions, will also dissolve in an excess of common cations.

One of the most widely studied precipitates in this connection is mercuric iodide. HgI_2 is one of a series of complexes HgI^+, HgI_2, HgI_3 and HgI_4^{2-}. Morse [4] who demonstrated the formation of all the complexes in this series, also determined the constants in the stepwise dissociation of $HgCl_4^{2-}$. The solubility of HgI_2 in excess of common anions is well known. KI dissolves almost an equivalent amount of HgI_2. In addition, HgI_2 dissolves in excess of $Hg(NO_3)_2$, forming the complex HgI^+:

$$HgI_2 \text{ (solid)} + Hg^{2+} = 2HgI^+.$$

According to Morse, 48 g of HgI_2 (i.e., ca. 0.105 mole) can be dissolved in 1 liter of N $Hg(NO_3)_2$.

AgI dissolves both in excess KI and in excess $AgNO_3$, forming the complex cation Ag_2I^+. Similar reactions can be observed with other precipitates (BiI_3, etc.)

The solubilities of the oxalates of the rare earths and of thorium are of great importance in the determination of these elements. In work published on the solubility of rare earth and thorium oxalates, and also in published methods for the analyses of these elements, it is emphasized that these oxalates must only be precipitated by oxalic acid, and not by the oxalates of the alkali metals, since the latter form soluble complexes. The rare earth oxalates in this connection are therefore analogous to $Al(OH)_3$, which must be precipitated by a weak base, NH_4OH, since it will dissolve if there is a considerable excess of OH' ions present. The slightly dissociated oxalic acid (in the presence of HCl) gives a low concentration of $C_2O_4^{2-}$ ions, which are sufficient for the quantitative precipitations of the rare earth oxalates. On addition of the highly dissociated oxalates of the alkali metals however, soluble oxalate complexes of the rare earths and thorium are formed.

In view of the properties noted above of precipitates of a complex character, it is to be expected that rare earth oxalates would also dissolve in excess of common cations. In fact, the oxalates of cerium and thorium dissolve easily (particularly on heating) with the formation of complex cations $Ce_2O_4^+$, $ThC_2O_4^{2+}$, etc., when the precipitates are treated with solutions of cerium or thorium nitrates, respectively. Similar reactions with the iodates of certain rare earths are sometimes used as a proof of the incorrectness of the solubility product principle. However, a study of the effect of other electrolytes shows that if these electrolytes do not react chemically with the precipitate, then their effect will be insignificant (for the same ionic strength of the solution). The solubility of precipitates as a result of the formation of complex cations is of no less significance than the solubility owing to the action of excess anions, although the first group of reactions has been studied to a considerably less extent. The enhanced solubility of the oxalates of thorium, and of the rare earths, in the presence of salts of aluminum, and particularly of iron, is due

to the formation of complex cations of the type $AlC_2O_4^+$, $FeC_2O_4^+$, and also $ThC_2O_4^{2+}$ etc. Precipitated CaF_2 dissolves easily in excess $AlCl_3$, the complex cation AlF^{2+} (or AlF_2^+) being formed.

Changes in the Solubility of a Precipitate of a Complex Character in the Presence of Common Ions

The examples of complex formation between precipitates and common ions in solution noted above, necessitate consideration of the general question of the change in solubility owing to the action of excess common ions.

HgI_2 can be taken as a characteristic example of such a system in which complex formation occurs. As mentioned above, a series of complex groups HgI^+, HgI_2, HgI^{3-} and HgI_4^{2-} can be formed in the system $KI - Hg(NO_3)_2$ in solution, depending on the absolute and relative concentrations. According to experimental results obtained by Morse [4] which have been somewhat modified by the present author [5], the formation of complexes in the system $Hg^{2+} - I^-$ (in solution) is characterized by the following relations for the stepwise dissociation constants.

$$K_1 = \frac{[Hg^{2+}][I^-]}{[HgI^+]} = 10^{-14}; \qquad K_2 = \frac{[HgI^+][I^-]}{[HgI_2]} = 10^{-10.3};$$

$$K_3 = \frac{[HgI_2][I^-]}{[HgI_3^-]} = 10^{-5.3}; \qquad K_4 = \frac{[HgI_3^-][I^-]}{[HgI_4^{2-}]} = 10^{-0.7}.$$

The solubility of HgI_2 in water is $1.4 \cdot 10^{-4}$ mole per liter. On the basis of these results, it is possible to calculate the state of HgI_2 in a saturated aqueous solutions

The principle of calculation is similar to the well known formula for the pH of an acid salt and consists of the following. The dissociation of HgI_2 in solution, in accordance with the values of the stepwise dissociation constants, proceeds mainly according to the equation $2HgI_2 = HgI^+ + HgI_3^-$; the ions Hg^{2+} and I^- are formed only to an insignificant extent.

So that the solution remains electrically neutral

$$[HgI^+] = [HgI_3^-].$$

From the relations for K_2 and K_3, it is found that

$$[HgI^+] = \frac{K_2 \cdot [HgI_2]}{[I^-]} \text{ and } [HgI_3^-] = \frac{[HgI_2][I^-]}{K_3}.$$

Comparing these equations, it follows that: $[I^-]^2 = K_2 \cdot K_3$, from which $[I^-] = \sqrt{K_2 \cdot K_3} = 10^{-7.8}$.

From the last relation and K_2 $\frac{[HgI^+]}{[HgI_2]} = \frac{K_2}{[I^-]} = \frac{10^{-10.3}}{10^{-7.8}} = 10^{-2.5}$,

i.e. the concentrations of HgI^+ (and HgI_4^{2-}) are very small in comparison with the concentration of the molecules of HgI_2, therefore it can be assumed that the concentration of the non-dissociated part of the HgI_2 is equal to the total solubility, i.e., $[HgI_2] = 1.4 \cdot 10^{-4}$. Using this value, and also the concentration of $[I^-] = 10^{-7.8}$ calculated above, it is possible by the usual methods (by means of the relations of the dissociation constants) to find the concentrations of the

residual components of the system. Omitting the details of calculations, the results are as follows (approximately).

In a saturated solution of HgI_2, the following concentrations of the different complexes are in equilibrium: $[Hg^{2+}] = 3\cdot10^{-13}$; $[HgI^+] = 5\cdot10^{-7}$; $[HgI_2] = 1.4\cdot10^{-4}$; $[HgI_3^-] = 5\cdot10^{-7}$; $[HgI_4^{2-}] = 4\cdot10^{-14}$; $[I^-] = 1.4\cdot10^{-8}$.

The existence of such a complicated system in equilibrium in a saturated solution is not exceptional. Analogous results can be found in the literature for other electrolytes, e.g., PbI_2, etc. The equilibrium system in a saturated solution of Na_3AlF_6, is undoubtedly even more complex [6]. In this connection, it is essential to ask how to express the solubility product of a precipitate of a similar type. In a saturated solution of HgI_2, five types of ions can be found apart from the undissociated molecule of HgI_2. The concentration product of any pair of ions which can form HgI_2 by interaction, will be a constant, and can with equal justification be regarded as the solubility product. Thus, the precipitate of HgI_2 can be formed by the interaction of $Hg^{2+} + 2I^- = HgI_2$. The constant for this reaction is given by

$$\underline{Lp}_1 = [Hg^{2+}]\cdot[I^-]^2 = 6\cdot10^{-29}.$$

The formation of a precipitate is also possible as a result of the reaction $HgI^+ + I^- = HgI_2$. The second "solubility product" corresponds to this equation:

$$\underline{Lp}_2 = [HgI^-]\cdot[I^-] = 7\cdot10^{-15}.$$

Other relations for the "solubility product" are also possible, each of which will have a constant value in a saturated solution. The question is which of these expressions will be the "true" solubility product. This question has no real significance for a system in which complex formation occurs.

In a system where there is no complex formation, it is possible to calculate the solubility of a precipitate in the absence of common ions, by means of the solubility product. In a given case, as can be seen from the values given above, the solubility is determined not by ions, but by the presence of undissociated molecules of HgI_2.

In a system where there is no complex formation, it is possible to calculate the decrease in solubility, on increasing the concentration of one of the ions, from the values of the solubility product. In the case considered, even complete elimination of the ionic solubility cannot essentially lower the solubility of the precipitate, since the concentration of the precipitate ions is negligible in comparison with the concentration of molecules of HgI_2. Moreover, the addition of complex ions (such as HgI_3^-) has no practical significance, while the introduction of simple ions (Hg^{2+} and I^-) will increase the solubility. The relations $\underline{Lp}_1$, $\underline{Lp}_2$, etc., given above characterize the free energy of formation of the solid phase from the corresponding ions. However, it is neither one nor the other of the relations for the solubility product which is important for the characterization of the equilibrium between the solution and a precipitate of complex nature. A knowledge of these values (and also of the solubilities of the precipitate) enables the effect of the common ion to be calculated.

For the precipitate of HgI_2 (and other precipitates of a similar type) the solubility in the presence of excess common ions can be found from the following equations. The solubility in the presence of excess anions is determined by the formation of HgI_3^- according to the reaction $HgI_2 + I^- = HgI_3^-$.

From which, taking into account the third dissociation constant, the following relation is obtained:

$$[HgI_3^-] = \frac{[HgI_2]\cdot[I^-]}{K_3}$$

The solubility in the presence of excess cations is determined by the formation of HgI^+ according to the reaction $HgI_2 + Hg^2 = 2HgI^+$.

The solubility as a function of the varying concentration of the cations $[Hg^{2+}]$, the constant value of the molecular solubility $[HgI_2]$, and dissociation constants of the complexes, can be calculated from K_1 and K_2 by elimination of the value of $[I^-]$:

$$[HgI^+] + \sqrt{\frac{K}{K_1}[HgI_2][Hg^{2+}]} = \sqrt{\frac{K}{K_1}\,1.4\cdot10^{-4}\cdot[Hg^{2+}]}$$

By direct substitution of the values in the above equation, it is possible to show that the solubility for a 0.1 excess of ions will be $[HgI_3^-] = 3$, i.e. in practice, the solution of HgI_2 in KI proceeds until almost all the latter is used up. For an equal excess of cations, the solubility will be less; for $[Hg^{2+}] = 0.1$ mol., $[HgI^+] = 0.2$ (this approximates to Morse's results).

The minimum solubility for precipitates of the type of HgI_2, which occurs in the absence of excess common ions appears to be in complete contradiction with the properties of precipitates which cannot form complexes.

Actually, as was shown above, the solubility of HgI_2 is determined chiefly by the presence of molecules.[1] Consequently the lowering of the concentration of HgI^+ or HgI_3^- ions in the presence of common ions, is generally of no appreciable significance. On the other hand, complex formation increases the solubility even at very low concentrations of excess common ions, e.g., it is possible to calculate the concentration of common ions, for which the solubility doubles. This, obviously, will take place if the "additional solubility" i.e., the concentrations of $[HgI^+]$ or $[HgI_3^-]$ become equal to the concentrations of molecules of $[HgI_2]$, in a saturated solution. For the condition where $[HgI^+] = [HgI_2]$, then $[I^-] = K_3 = 5\cdot10^{-6}$; while for $[HgI^+] = [HgI_2]$, $[Hg^{2+}] = \frac{K_1}{K_2}$, and $[HgI_2] = 3\cdot10^{-8}$. Thus even at a very low excess of common ions the solubility increases to double the value of the solubility in pure solvent.

For many precipitates the capacity of complex formation is not so manifest as for HgI_2. Thus, according to some results in the literature and to the author's calculations, the solubility of PbI_2 is determined chiefly by the presence of Pb^{2+} and I^- ions, in addition to which there are only 10% PbI^+ ions and even less PbI_2 molecules. The solubility of such compounds, which seem to be a more general type of precipitate, can be characterized as follows. The curve relating the total solubility of the precipitate to the concentration of an excess of anions of the same kind, may be expressed as the sum of two curves for the different kinds of solubility. One form of solubility ($\underline{X}_1$) is determined by the presence of simple ions, and can be calculated by the normal method from the solubility product. This part ($\underline{X}_1$) of the total solubility decreases on adding similar ions.

The other form of solubility ($\underline{X}_2$) is determined by the formation of complexes

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[1]) Results collected in handbooks on solubilities also indicate that the solubility of HgI_2, as determined gravimetrically, is a few hundred times the solubility calculated from electro-conductivity measurements.

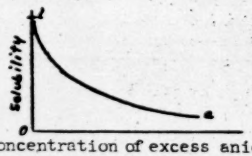
with common ions. This form of solubility increases on introducing excess of common ions.

The total solubility will be equal to $S = X_1 + X_2$. For a small excess of anions X_2 will be small (complex formation is insignificant), and the solubility will be determined chiefly by the value of X_1. On increasing the concentration of the excess of common anions, the value of X_1 decreases in accordance with the solubility relation. On the other hand, the value of X_2 gradually increases (particularly as the value of [A] approaches the value of K_3) and finally becomes greater than the value of X_1. Thus, the relation between total solubility and the concentration of excess common anions is expressed by a curve with a minimum. From what has been said above, it is obvious that the minimum will occur when $X_1 = X_2$. Korenman [7] came to similar conclusions for the solubility of PbI_2 in KI. Lanford and Kiel [6], during detailed investigation on the solubility of PbI_2 in KI, also found a similar minimum (at 0.1 M KI). If the dissociation constant of the complex $K_{BA_3} = \frac{[B^+][A^-]^3}{[BA_3^-]}$, then according to Korenman's calculations the solubility minimum will occur at $[A^-] = \sqrt[3]{K_{BA_3}}$. In connection with the results given above for the stepwise character of the formation of the complexes, the relation between the solubility of the precipitate and excess of cations will be characterized in similar cases by a curve having a minimum.

The General Characteristic of the Effect of Common Ions on the Solubility of Precipitates, when Complex Formation Occurs

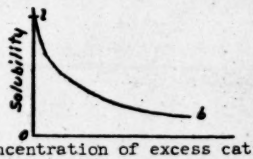
From the characteristics of the equilibrium between precipitate and excess of common ions considered above, it is possible to make a number of general conclusions. The normal character of a precipitate - the solubility product - can be used for calculating the solubility in the presence of excess common ions, only when there is no complex formation. For many precipitates, on the other hand, the formation of complex anions and cations by the action of excess common ions is, to one degree or another, characteristic. In order to calculate this effect, it is essential to know the values of the stepwise dissociation constants of all the complexes formed in the system. These values are known for only a few cases. Such calculations, though of interest in individual typical cases, cannot be used in the study of the formation and solution of many precipitates. It is more expedient therefore to characterize such complex equilibriums on the basis of physico-chemical analysis.

Usually during investigation of the effect of common anions on the solubility of the precipitate, the results are expressed by a digram of the type shown in Fig. 1.



Concentration of excess anions A.

Fig. 1.



Concentration of excess cations B.

Fig. 2.

Solubility is plotted along the ordinate, and the concentration of excess A anions along the abscissa. The point 0 corresponds to a pure precipitate in the absence of excess common ions, and the ordinate 01 represents the solubility of the precipitate under these conditions. If, e.g. the precipitate does not form, or only forms an unstable complex with excess A anions, then the relation between the solubility of the precipitate and the concentrations of A anions is depicted by the lina 1a curving downward.

The results of investigating the solubility of a precipitate in the presence of excess common cations are usually expressed in the manner shown in Fig. 2. The concentration of ions and the solubility of the precipitate are plotted against the abscissa and ordinate respectively. In the absence of any appreciable complex formation, the relation is expressed by the descending curve 1b. When however, this method is used for plotting the results, such properties of the precipitate as are closely related and are determined by the chemical nature of the precipitate, are considered separately. During the precipitation of any precipitate, there exists initially a system with an excess of one of the anions, while toward the end of precipitation (after the addition of an equivalent amount of precipitant) the system contains an excess of the second ion. Sometimes the same precipitate (e.g. AgCl) can be used for determining either the cation or the anion, under different conditions. Therefore it is worth while combining the two types of diagram so as to consider in a general way the effect of both ions on the solubility of the precipitate. To do this, Fig. 2 is turned around the ordinate through 180° and placed back to back to Fig. 1, to give a diagram of the type of Fig. 3, which under certain additional conditions [1]) will be a typical diagram of physico-chemical analysis, and characterizes the relation between the composition and a property of the system. The ordinate represents the most important property of a precipitate – its solubility – while the abscissa represents the different possible concentrations of excess of both common ions.[2])

The formation of a precipitate in a saturated solution containing excess ions of both types can be effected simply by mixing a solution of electrolyte containing the cation B with a solution of an electrolyte containing the anion A. The original solutions can be prepared of equal molarity and can then be mixed in different amounts, so that the sum of the volumes of the solutions remains a constant. In reactions between ions of the same valency, a precipitate BA is normally obtained. If, e.g. 50 ml of a salt of B is mixed with 50 ml of a solution of a salt of A (solutions of equal molarity), then a system is obtained in which the precipitate is completely free of excess of common ions. The geometrical position of a mixture composed of equal volume of A and B correspond to point 0 on the abscissa of the composition-property diagram (Fig. 3). The ordinate at this point, 01 represents the solubility of the precipitate in the absence of common ions. It is obvious that 01 (Fig. 3) in the physical sense corresponds to similar ordinates in Figs. 1 and 2.

If solutions of the reactants are not mixed in equivalent amounts, then the mixture will correspond to different points along the abscissa. Systems of precipitate BA in the presence of different concentrations of excess anions A lie to the right of 0, while systems of precipitate BA in the presence of different concentrations of excess common cations B lie to the left of 0. The relation between solubility and concentration of excess ions is expressed by the charac-

[1]) It is the relative and not the absolute values of the concentration or volume which are plotted on the abscissa. The scale is also changed.
[2]) I.V.Tananaev used a similar diagram.

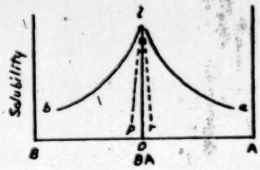


Fig. 3

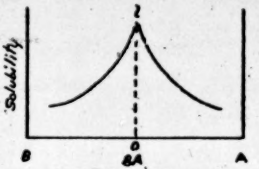


Fig. 4

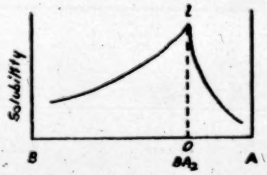


Fig. 5

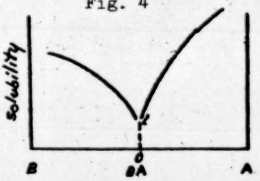


Fig. 6

teristic curve b1a. The curvature of the lines bl and la depend on the choice of scale and units of measurement on the coordinate axes. For general characterization of a precipitate and also for the classification of precipitates, the question of scale is immaterial, and it is possible to use an arbitrary scale, which only indicates the principal trend of the relation.

The necessity of classifying precipitates according to the character of the effect of similar ions has been remarked on in the literature, e.g. in Golovatov's work [9]. Similar ideas regarding the various relations between solutions and excess of common ions have been put forward by I. V. Tananaev [10]. However, in accordance with the results given above, the solubilities of a series of precipitates in the presence of excess common ions is not connected with their high valency, since this is observed for such precipitates as AgCN, HgI_2, etc.,. The increase in solubilities is determined by chemical interaction with the formation of complex ions. On the basis of the results of an experiment represented on a diagram of the type of Fig. 3, it is possible to determine the character of the interaction between the precipitate and each of the common ions, and to simplify the calculation of the different constants (Lp and K complex). Finally, the application of such diagrams, with the help of additional curves (e.g., the dotted lines lp and lr), enables observations of the change in composition of the solid phase, owing to the formation of mixed crystals, etc., to be made.

According to the character of the effect of the common ions it is possible to distinguish four types of precipitates, to which characteristic forms of the composition-property diagram correspond.

1. The absence of complex formation between ions of the precipitate. This type of precipitate is the "ideal" one for use in analysis, since excess of common ions decreases the solubility of the precipitate, in complete agreement with the relation Lp. This curve is characterized by a sharp maximum at the point corresponding to the composition of the precipitate (Fig. 4). The form of the curve depends on the choice of scale (simple or logarithmic) and also on the composition of the precipitate. In the case of a precipitate of composition BA both branches of the curve are symmetrical (Fig. 4); for a composition BA_2 the excess of anions decreases the solubility more than an excess of cations, Fig. 5.

2. Strong complex formation between precipitate ions, in which the precipitate is a compound which is unsaturated in the coordination sense (Type HgI_2). In this case the curve has a form directly opposite to the previous curves. A point on the curve 1, corresponding to the precipitate, i.e. to the absence of excess common ion, represents the minimum solubility (Fig. 6). Excess of each of the components increases the solubility.

3. Strong complex formation, in which the precipitate is a compound saturated in the coordination sense. The relation between the solubility of cryolite, Na_3AlF_6, and the concentration of aluminum and fluorine ions can be taken as a typical example of this class.[1] If there is a complex group, e.g. Ba_2, in this precipitate (for a maximum coordination number for B of 4), then the relation will have the form illustrated in Fig. 7. Excess of anions A cannot lead to the formation of new complexes, and will therefore lead to a sharp decrease in the solubility of the precipitate. On the other hand, excess of ions B will react with the precipitate, forming coordinately unsaturated complexes BA_3, BA_2 and BA, as a result of which the solubility of the precipitate will increase.[2]

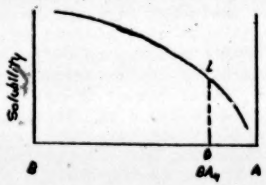


Fig. 7

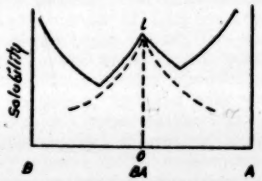


Fig. 8

4. Weak complex formation between precipitate ions. It is apparent that most real precipitates belong to this class. In general, the relation between precipitate solubility and excess common ions is represented by a curve with a maximum in the absence of common ions, and with two minimums in the presence of excess common ions (Fig. 8). For a low excess of common ions there is a decrease in solubility of the precipitate, although the decrease is not so great as would be expected on the basis of the usual application of the solubility product (dotted line, Fig. 8). For a large excess of common ions, complex formation becomes the dominant process and the solubility begins to increase. This type of common ion effect is observed for PbI_2 in the presence of excess KI, and in many other cases.

When complex formation is very weak, the minimums can lie very near to the ordinate. In some cases, when the solubility of the original salt containing B and A is restricted, the minimums cannot be observed at all; however, the solubility will be slightly higher tha that calculated from the normal solubility product (L_s). In such cases, the general expression for solubility product can be used for approximate calculation, but only within the limits of concentration, corresponding to the interval between the two minimums on the curve.

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1) The complete relation between the concentrations of all the ions of such a precipitate, i.e. the concentrations of Na^+, Al^{3+} and F^+, must be expressed by a ternary diagram.

2) Thus, the solubility of cryolite in aluminum salts, the solubility of the hydroxyquinolates of a series of multivalent metals in the presence of an excess of the cations of these metals, etc. are well known.

SUMMARY

The effect of common ions and other ions on the solubility of precipitates has been considered. The ionic strength of the solution has some effect, but it is not large, and can be eliminated by using solutions of equal ionic strength, which correspond to practical analytical conditions. The most important effect is that of the chemical interaction between solid phase and ions in solution.

The effect of common ions on the solubility of the precipitate has been considered, when complex anions and cations are formed in the presence of excess precipitant. For precipitates which in their chemical character are one of a series of stepwise complexes in the system B cations – A anions, the solubility product is not single valued and cannot be use for the calculation of solubility.

The importance of using the principles of physicochemical analysis for characterizing the changes in solubility owing to the action of excess of similar ions has been pointed out. For this purpose, a diagram of composition against property can be used, in which the components of the composition are the solutions of the reacting ions, while the solubility of the precipitate is taken as the most important property of the system. On this basis, precipitates can be divided into four classes: 1) the absence of complex formation is characterized by maximum solubility at the equivalence point; 2) strong complex formation, characterized by minimum solubility at the equivalence point (in the absence of excess common ions); 3) complex formation, under conditions in which the precipitate is a coordinately saturated compound, in this case excess common anions, decreases the solubility, while excess common cations increases the solubility; 4) the solubilities of a large number of precipitates is expressed by a curve with a maximum in the absence of common ions, and with two minimums for a definite excess of each of the common ions.

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PHYSICO-CHEMICAL ANALYSIS OF SYSTEMS OF IMPORTANCE IN ANALYTICAL CHEMISTRY[1)]

XX. THE SOLUBILITY OF PRECIPITATES IN COMPLEX (REAL) ANALYTICAL SYSTEMS

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The present work is a continuation of the authors' work on the study of the solubility of $PbSO_4$ in solutions of different electrolytes, the ions of which are the same as, or differ from those of the precipitate, and the cations of which are of different valency [1]. The noteworthy feature of the systems $PbSO_4$ – $Th(NO_3)_4$ – H_2O and $PbSO_4$ – $Th(NO_3)_4$ – Li_2SO_4 – H_2O, which is considered in the present article, is the presence of the nitrate of a quadrivalent cation. As far as the authors are aware there is no description of these systems in the literature, neither are there any experimental results relating to the errors which arise when calculating solubility on the basis of the constancy of La (the activity product), and the values of the activity coefficients are calculated from the Debye-Huckel equation. In so far as firstly the ionic strength of the solution is taken into account in the Debye-Huckel equation, while secondly the chemical interaction between the dissolved ions and precipitate is neglected, it is to be expected that disagreement between experiment and theory will be particularly large in the systems considered. The first is determined mainly by hydrolysis and incomplete electrolyte dissociation in solution, while the second is determined by the enhanced chemical activity usually observed for multivalent cations, which form chemical bonds of varying stability with the majority of anions. The nitrate of thorium was chosen as the quadrivalent cation because aqueous solutions of this salt are stable without the addition of acid. Lithium sulfate was chosen as the electrolyte containing a common ion, because as was shown previously [2, 4], $PbSO_4$ in the presence of lithium ions does not change its composition, when it comes into contact with a solution containing excess sulfide ions.

The determination of the concentration of lead in the saturated solutions was made by the use of a Chromate-iodometric method with preliminary precipitations of lead sulfide from tartaric acid solution.

In experiments on the determination of the solubility of $PbSO_4$, the concentrations of $Th(NO_3)_4$ varied from 0.0001 to 0.1 molar, for a constant concentration of Li_2SO_4 in a given series of experiments. Three lots of systems were investigated in which the concentrations of Li_2SO_4 were 0.001, 0.01 and 0.1 molar; one series was done in the absence of Li_2SO_4.

The activity coefficients according to the Debye-Huckel equation (second approximation) were calculated on the assumption of the constancy of La in all cases, on the lines of a method worked out previously. The necessary values of a were found by starting not from 0.1 and molar solutions of the electrolyte (as before) but from 0.01 and 0.1 molar solutions of $Th(NO_3)_4$ respectively.

1) Report read at the Conference on Classical Methods of Chemical Analysis held in Moscow 14-17 Nov. 1951.

TABLE 1

The Solubility of $PbSO_4$ in the system $PbSO_4 - Li_2SO_4 - Th(NO_3)_4 - H_2O$ at 25° C

$Th(NO_3)_4$ molar	Li_2SO_4 = 0.0 molar: Pb mol/l · 10^4	$La_{PbSO_4} \cdot 10^8$	$La_{PbSO_4} \cdot 10^8$ For a equal to 3.04	4.86	0.27	Li_2SO_4 = 0.001 molar: Pb mol/l · 10^4	$La_{PbSO_4} \cdot 10^8$	$La_{PbSO_4} \cdot 10^8$ For a equal to 3.04	-4.88	-0.26
0.0001	8.18	66.9	37.8	33.9	36.5	3.32	44.2	23.5	19.8	21.6
0.001	22.4	502	163	96.9	137	13.5	317	125	63.1	88.4
0.01	103	10600	835	1.62	1090	84.2	7930	644	1.62	227
0.1	289	83500	702	0.059	1.62	276	78900	665	0.063	1.62

From Table 1, it is obvious that $Th(NO_3)_4$ strongly increases the solubility of $PbSO_4$, the solubility in 0.1 molar $Th(NO_3)_4$ being 200 times that in pure water. This increase is considerably more than was found previously for $Al(NO_3)_3$ [1]. In the presence of Li_2SO_4 the effect of $Th(NO_3)_4$ on the solubility of $PbSO_4$ varies with the concentration of the Li_2SO_4, being less the greater the concentration of Li_2SO_4.

Fig. 1 (given in two scales for convenience) and particularly Fig. 2 illustrate this very graphically. Only in 0.1 molar Li_2SO_4 does the solubility of $PbSO_4$ approach the value characteristic for pure water, although this is true only for concentrations of $Th(NO_3)_4$ not higher than 0.01 molar; for 0.1 M $Th(NO_3)_4$ the solubility of $PbSO_4$ is still 10 times that in water. For low concentrations of Li_2SO_4 the solubility of $PbSO_4$ increases sharply, as shown in Fig. 2 by the dotted lines, which are lines of equal concentrations for $Th(NO_3)_4$. This is especially marked for lines of equal concentration for 0.1 molar $Th(NO_3)_4$. As can be seen from Table 1 the calculation of La_{PbSO_4} did not give good results. It follows therefore that in systems of the type considered, the formulas used do not give correct values for the activity coefficients, without which the principle of the constancy of La cannot be used. The negative value of a which is devoid of any physical meaning, is characteristic.

The above deviations are explained by the presence in the system of a clearly expressed chemical affinity, manifested in the formation of slightly dissociated ions, apparently of the type of $ThSO_4^{2+}$. It is therefore more correct to calculate the solubility of $PbSO_4$ from the dissociation constant of such ions, the results obtained being superior to those obtained by calculations based on the use of the activity coefficients of the dissolved precipitate, which as a rule (particularly in complex systems) are unknown and are difficult to determine. In the present work, calculations based on this principle were not made because of insufficient experimental data for intermediate concentrations of $Th(NO_3)_4$.

On the other hand it should be noted that the solubility diagram adduced, enables the solubility of $PbSO_4$ to be found for any part of the system studied, with a fairly close approximation to the true value. The diagram can be used for practical purposes in cases where it is necessary to precipitate lead in the presence of multivalent ions.

The Solubility of Precipitates Under Real Analytical Conditions

The composition of solutions in systems which are dealt with in the course of chemical analysis is usually complex. Ions both common to and different from

TABLE 1

The Solubility of $PbSO_4$ in the system $PbSO_4 - Li_2SO_4 - Th(NO_3)_4 - H_2O$ at 25°C

Li_2SO_4 = 0.01 molar					Li_2SO_4 = 0.1 molar				
		$La_{PbSO_4} \cdot 10^8$ For a equal to					$La_{PbSO_4} \cdot 10^8$ For a equal to		
		3.04	-4.11	-0.186			3.04	-0.75	0.355
1.25	126	21	14.4	23.7	0.57	560	21	1.54	4.84
1.28	128	27	9.75	19.2	1.36	1360	49	0.33	1.05
13.1	1480	121	1.62	44.7	1.74	1740	47	1.62	7.24
194	57000	483	0.60	1.62	18.8	19200	137	0.0069	1.62

the precipitate ions enter into the composition. It is often difficult to resolve the question of the solution of precipitates under such conditions by theoretical calculations. This is explained by the variety of possible reactions between the ions composing the solutions and precipitate, and the variety of processes underlying precipitate solubility in each individual case.

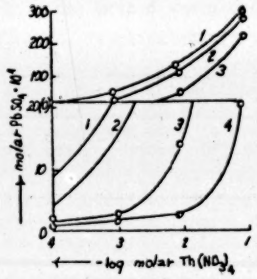

Fig. 1 - Solubility in the system $PbSO_4 - Li_2SO_4 - Th(NO_3)_4 - H_2O$ [Li_2SO_4]: 1 - 0.0 molar; 2 - 0.001 molar; 3 - 0.01 molar; 4 - 0.1 molar

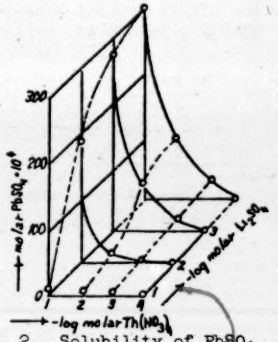

Fig. 2. Solubility of $PbSO_4$ in the system $PbSO_4 - Li_2SO_4 - Th(NO_3)_4 - H_2O$.

On the basis of literature results and of our own work on the study of precipitate solubility, we concluded that at the present time a universal method of calculating the solubility in complex systems is hardly feasible.

As shown previously and in the present work the calculation of precipitate solubility on the basis of the constant La is rendered difficult owing to the absence of results on the activity coefficient in complex systems. Calculation of activity coefficients according to the Debye-Huckel equation (second approximation), gives good results in many cases; however, in the presence of any appreciable chemical affinity in the system, this method becomes unsuitable.

As I. V. Tananaev and Deutchman [2] showed during the study of solubilities in the systems — metal fluorides (LiF, CaF_2, $PbFCl$) — $Be(NO_3)_2$ — H_2O, where chemical affinity is clearly manifested, that precipitate solubility can be calculated with a fairly good approximation to the true value, by the use of the values of the dissociation constants of the products formed in solution (in this case BeF^+) and of Lp in its usual form.

A similar conclusion was made above, in connection with the study of the solubility of $PbSO_4$ in the presence of $Th(NO_3)_4$ (formation of $ThSO_4^{2+}$).

An experiment in the application of physico-chemical analysis in the study of analytical systems containing precipitates showed us that these systems are usually considerably more complex than is normally assumed. Apart from the phenomena mentioned above, the precipitate itself very often changes its compositions owing to the formation of double (complex) salts, or solid solutions, so that any approach to the problem which does not take into account this aspect of the question, loses its justification and significance.

In spite of this, however, it seems that on the basis of the large amount of experimental data on the study of all possible forms of systems by the solubility method, it is possible at present to draw up a qualitative classification of systems containing precipitates, by means of which it will be possible to predict the direction of the process. For this purpose a diagram of the solubility of the precipitate in the presence of an electrolyte containing a common ion is used. This method was proposed by one of the authors [3] [1].

The diagram, represented by Fig. 3 illustrates the following types of systems. [2]

Type 1,1. Systems in which salting out of the precipitate (decrease in solubility) occurs on both the anion and cation sides. The effect of ions not common with precipitate ions is small. Complex formation is absent both on the anion and cation sides ($TlCl + Tl^+$; $TlCl + Cl^-$; $BaSO_4 + Ba^{2+}$; $BaSO_4 + SO_4^{2-}$).

Type 2,2. Partial salting out on the cation and anion sides with subsequent complex formation (increase in solubility) on both sides. The curves as a rule are unsymmetrical ($AgCl + Cl^-$; $AgCl + Ag^+$; $MgC_2O_4 + Mg^{2+}$; $MgC_2O_4 + C_2O_4^{2-}$).

Type 3,3. Strong complex formation on the cation and anion sides [$Th(C_2O_4)_2 + Th^{4+}$; $Th(C_2O_4)_2 + C_2O_4^{2-}$].

Type 1,2. Salting out and the absence of complex formation on the common cation side, and partial salting out with subsequent complex formation on the common anion side ($AgNO_2 + Ag^+$; $AgNO_2 + NO_2^-$).

Type 1,3. Salting out on the side of the cation, and strong complex formation on the anion side ($AgCN + Ag^+$; $AgCN + CN^-$).

Type 2,1. Partial salting out with subsequent complex formation on the side of the cation, and only salting out on the anion side ($MgF_2 + Mg^{2+}$; $MgF_2 + F^-$; $PbSO_4 + Pb^{2+}$; $PbSO_4 + SO_4^{2-}$).

1) Reported by I. V. Tananaev at the meeting of the Scientific Council of the Institute of General and Inorganic Chemistry, Academy of Sciences USSR in 1943.

2) In these examples only the salt components of the system are indicated.

Type 2,3. Partial salting out with subsequent complex formation on the cation side, and strong complex formation on the anion side [$Al(OH)_3 + Al^{3+}$; $Al(OH)_3 + OH^-$].

Type 3,1. Strong complex formation on the cation side, and salting out on the anion side ($ThF_4 + Th^{4+}$; $ThF_4 + F^-$).

Type 3,2. Strong complex formation on the cation side, and partial salting out with subsequent complex formation on the anion side.

From the examples quoted above it is obvious that the curves can have the most diverse shapes, from curves having maxima (types 1,1; 1,2; 2,1) to curves having minima (type 3,3). Curves can also be obtained which do not intersect on the ordinate and correspond to the precipitate solubility in pure water (types 3,1 and 1,3). All this variety of curves is explained by the fact that the solubility of the precipitate is determined by processes which are mutually opposed, namely the salting out effect and complex formation. In this connection it is possible to imagine a limiting case where the solubility of the precipitate is expressed by a straight line parallel to the abscissa (the dotted line on Fig. 3), in such a case salting out and complex formation mutually compensate each other. Cases of pure salting out or complex formation respectively are rarely met. Salting out of $AlCl_3 \cdot 6H_2O$ or $BaCl_2$ by gaseous HCl is an example of the former, while the reaction $AgCN + CN \longrightarrow [AgCN]_2$ typifies the second.

The classification given above based to a considerable extent on the difference between systems, which arise from the ionic types of the individual components of these systems, indicates to a first approximation only part of the question of precipitate solubility. Fig. 3 represents such a system when the composition of the precipitate remains unchanged and corresponds to a simple salt. In the majority of cases however, changes occur in the precipitate as the result of various processes, in particular the formation of double salts or solid solutions. In such cases it is necessary to consider the whole diagram, in which every new phase is represented by the corresponding curve (branch) of solubilities.

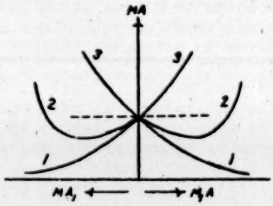

Fig. 3. Solubility of a salt (MA) in the presence of electrolytes with common ions (M,A and MA_1)

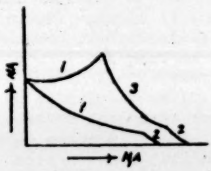

Fig. 4. Solubility of the precipitate (MA) in the presence of electrolyte (M,A)
1 – MA; 2 – M_1A; 3 – $M_1[MA_2]$

The type of diagram which is obtained for the simplest case where one double salt occurs together with complex formation (on the anion side) is represented in Fig. 4. However, in many cases several new solid phases appear and the form of the diagram becomes correspondingly more complicated. A number of such cases are described in the literature. In particular the following systems may be mentioned: AlF_3–NaF–H_2O, in which $11NaF \cdot 4AlF_3$ and $AlF_3 \cdot 3NaF$ [4] separate out; FeF_3–KF–H_2O and AlF_3–KF–H_2O in which $FeF_3 \cdot 2KF \cdot H_2O$; $11KF \cdot 4FeF_3 \cdot 12H_2O$; $FeF_3 \cdot 3KF \cdot 3H_2O$; $AlF_3 \cdot 2KF \cdot H_2O$ and $AlF_3 \cdot 3KF$ can exist; [5,6]: $PbSO_4$–K_2SO_4–H_2O in which $PbSO_4$ and $PbSO_4 \cdot K_2SO_4$ separate out [7]: of particular interest in this connec-

tion are systems which contain insoluble ferrocyanides. Thus in the system $CoSO_4$-$K_4Fe(CN)_6$-H_2O, $5Co_2Fe(CN)_6 \cdot K_4Fe(CN)_6$ and $4Co_2Fe(CN)_6 \cdot 3K_4Fe(CN)_6$ separate out [8]; in the system $CoSO_4$-$Na_4Fe(CN)_6$-H_2O the following are formed $Co_2Fe(CN)_6$; $10Co_2Fe(CN)_6 \cdot Na_4Fe(CN)_6$; $3Co_2Fe(CN)_6 \cdot Na_4Fe(CN)_6$ and $2Co_2Fe(CN)_6 \cdot Na_4Fe(CN)_6$ [9]; in the system $CdSO_4$-$K_4Fe(CN)_6$-H_2O the compounds $5Cd_2Fe(CN)_6 \cdot 4K_4Fe(CN)_6$ and $Cd_2Fe(CN)_6 \cdot K_4Fe(CN)_6$ [10] are formed.

These examples of systems containing fluorides and ferrocyanides (which are not exceptions) show that systems containing precipitates can be very complex. Thus, in a number of the above systems, solid solutions were found as well as the slightly soluble double salts [1,11]. It is possible that in systems consisting of multivalent ions, hydrolysis also occurs with the formation of basic salts of different composition. This last possibility which leads to a complication of the picture as a whole, is not usually taken into consideration for the sake of further simplifications which are not always justified.

In the present article it is not proposed to give an exhaustive list of systems, in which a complex picture of the precipitation process is observed. This question is touched upon in the article of I. V. Tananaev already cited [3].

The aim of the present article, of necessity short, is to show that it is difficult to apply either one method or another of calculating the solubility of precipitates by means of Lp or La, to many analytical systems of practical importance which contain precipitates.

Table 2

Solubility of CaF_2 in the system CaF_2-$Al(NO_3)_3$-H_2O at 25°C.

$Al(NO_3)_3$ molar	$[Ca^{2+}]$ molar in satd. solution	$[F^-]$ total $[Al(NO_3)_3]$ in satd. solution	$K_{AlF_2^+} \cdot 10^{+}$
0.3	0.0524	0.35	2.34
0.1	0.0317	0.63	2.10
0.01	0.00681	1.36	2.40
0.003	0.00244	1.63	2.94
0.001	0.00096	1.92	1.38

In many cases the details of which forms of a particular compound exist in the solid phase and in solution are still uncertain. Details of the interactions between these various forms are also unknown. A typical example is the hitherto little studied formation of soluble, positively charged, predominately multivalent, metal ions containing unsaturated acido groups (left part of the diagram in Fig. 3. As we have shown previously [1] and in the present article, the solubility of a precipitate in such cases can be calculated on the basis of the dissociation constants of the slightly dissociated compounds formed in solution. This can be illustrated by taking as an example, the solubility in the system CaF_2-$Al(NO_3)_3$-H_2O, in which clearly defined interaction occurs according to the reaction [3].

$$Al^{3+} + 2F^- \longrightarrow AlF_2^+ .$$

Results on the solubility of CaF_2 in solutions of $Al(NO_3)_3$ of different concentrations are given in Table 2.

The dissociation constants of AlF_2^+ can be calculated from the formula:

$$K_{AlF_2^+} = \frac{(Al^{3+}) \cdot (F^-)^2}{(AlF_2^+)} = \frac{[C_{Al(NO_3)_3} - (Ca^{2+})] \cdot \frac{I_{CaF_2}}{(Ca^{2+})}}{(Ca^{2+})}$$

It can be seen from Table 2 that the value of $K_{AlF_2^+}$ varies within the very narrow limits of $1.38 \cdot 10^{-9}$ to $2.94 \cdot 10^{-9}$ i.e. it is practically constant, although the concentration of $Al(NO_3)_3$ changes by 300 times.

It follows from this that the calculation of the solubility of a precipitate in the presence of a clearly manifest chemical affinity in the system, on the basis of the constancy of Lp, is possible with a fair approximation to the true value. In order to do this however, it is essential to have a clear idea of the composition of the compounds formed in solution.

What has been said in this review may be summarized as follows.

The problem of the solubility of precipitates in many practical systems, usually of complex composition, cannot be resolved at the present time on the basis of calculation, without recourse to all sorts of simplifications, and accepting the system as such and accepting changes in concentration of the components within wide limits and changes in the compositions of the precipitate (formation of double salts, solid solutions,etc.). The fullest information about the behavior of systems containing precipitates can be obtained by the study of systems containing precipitates by means of the physico-chemical analytical method, with careful characterization of the composition of the solid and liquid phases. The most important reaction for practical systems is the exchange decomposition of the general type:

$$MeA + M_1A_1 \rightleftharpoons \underset{\text{precipitate}}{MeA_1} + M_1A$$

in which ions common to and different from the precipitate ions participate.

At the present time experimental results on the study of such reactions are extremely few and work along these lines should be regarded as one of the most pressing problems of analytical chemistry. Only on the basis of such work, in which investigation of the solubility of systems is carried out simultaneously with careful study of the chemical affinity of solutions by means of physico-chemical analysis, can a rational theory of precipitation reactions be developed in future, not to mention diagrams of solubility, in particular three dimensional diagrams which make it possible to choose, without any errors, the method of precipitation in analytical practice.

SUMMARY

Solubility in the system $PbSO_4$–$Th(NO_3)_3$–Li_2SO_4–H_2O at 25° has been studied. It has been shown that the Debye-Huckel equation cannot be used for calculating the solubility of $PbSO_4$ in this system, owing to a clearly manifested chemical interaction which is accompanied apparently by the formation of complex ions of the type $ThSO_4^{2+}$.

Some ideas have been put forward regarding the significance of physico-chemical analysis for the theory and practice of precipitation reactions, in connection with which a diagram is given of the type of ternary system: precipitate-electrolyte with common ion-water, which embraces all possible systems containing precipitates, in relation to the ionic type of the components and the character of the interaction process in the system.

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THE COMPLEX STUDY OF PRECIPITATES[1)]

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The formation of precipitates is a process which has been well known for a long time. Preparative and analytical chemistry, and factory practice have widely used difficultly soluble compounds. It is natural that a large amount of work has been devoted to this question, and many practical methods proposed, etc. Information on precipitates is to be found, e.g. in Kolthoff and Sandel's book on quantitative analysis [1].

The most common defect of many studies in this field is the absence of numerical values characterizing the precipitates themselves.

We have used a simple determination of the filtration coefficient, and studied a number of precipitates according to this and certain other properties [2]. We have made an attempt below to generalize the results obtained, using gypsum, and the hydroxides of magnesium iron and aluminum as examples.

Small crystals have the greatest solubility [1]; the velocity of solution depends on the difference between the actual concentration c'_2 of the precipitate in solution and the equilibrium concentration c'_1 in saturated solution of the precipitate.

If the difference $c'_2 - c'_1$ is large, then other conditions being equal, the solution velocity will be considerable and the small crystals will dissolve quickly while the coarse ones grow. On the other hand, a small value for $c'_2 - c'_1$ leads to a proportionate slowing down of this transfer, and leads ultimately to a continuous state of unbalance between fine and coarse particles.

During the separation of crystals from solution the difference $c_1 - c_2$ has an important effect, this is called the supersaturation and is the difference between the actual concentration c_1 of a given ion and the solubility of the precipitate c_2 coming out of solution. The greater the supersaturation, the higher the velocity with which the precipitate separates and the smaller the crystals formed. This is confirmed by many examples, in particular by Veimarn's work. It should be remembered that as precipitation proceeds c_1 falls and c_2 increases owing to the decrease in concentration of the original compound which has an ion in common with the precipitate. Obviously right at the end of precipitation (last drop) c_1 has for given conditions a minimum and c_2 a maximum numerical value respectively, i.e. the supersaturation $c_1 - c_2$ is a minimum.

The following methods can be used in order to attain minimum supersaturation for all precipitation processes: 1) decreasing c_1 (the use of dilute original solutions); 2) increasing c_2 to the maximum possible value (increasing the precipitate solubility); 3) decreasing c_1 and c_2 by the maintenance of conditions similar to those obtained during the addition of the last drop.

We shall briefly consider the effect of these methods on the precipitate.

1. A decrease in the concentration of both reagents can reduce the supersaturation many times over, and affect the distribution of particle size i.e. the quality of the precipitate e.g. according to Veimarn's results, on the addition of 0.001 N solutions of a sulfate to a barium salt of the same concentration, the precipitate of $BaSO_4$ appears after 5 minutes, the solution being clear up to that time. Precipitation lasts 2 hours and the particle size is 5μ.

[1)] Report read at the Conference on Classical Methods of Chemical Analysis held in Moscow, Nov. 14-17, 1951.

For a concentration of the reactants of 0.0002 N, the precipitate takes a month to form and the particle size is 30 x 15μ. Obviously this method is of no practical interest on account of the large volume of reactants and the slowness of the process.

2. The effect of increasing the solubility of the precipitate is also well known, e.g. in order to get coarse crystals of $Mg(OH)_2$, precipitation is carried out in the presence of NH_4Cl or sugar; good crystals of AgCl can be obtained by evaporation of an ammoniacal solution of this compound; calcium oxalate is precipitated from acid solution etc. Factory practice uses relatively concentrated solutions of sodium aluminate, which is spontaneously precipitated with separation of aluminum hydroxide (centrifuge method). Hoffer [3] on the basis of a study of the particle size of precipitates, gave an empirical equation $M = AL^2$, where M is the particle size of the precipitate, A is a constant and L is the solubility of the given compound, which is applicable to both easily soluble and difficultly soluble compounds. This equation only holds for comparable conditions of precipitate formation, in particular for the time of preparation.

3. The last drop method (Method A), is easily attained in practice by the addition of the two reactants dropwise, and separately, to a definite volume of water or other solution (buffer) [2].

It is important that as each drop of one reactant is added to the buffer it is thoroughly distributed before a drop of the other reactant is added. It is obvious that this technique requires careful regulation of the time of addition. By decreasing the volume of the drops added and increasing the volume of buffer, it is possible theoretically to get any given degree of supersaturation. This is a very effective method, because by means of such a method it is possible to organize a continuous process of precipitation and to pour very concentrated solutions into the buffer (see below).

In addition to the last drop method (Method A) the supersaturation may be decreased by adding dropwise a solution of the precipitant to the solution to be precipitated (Method B). This method is widely used in laboratory practice. In both Method B and to a lesser extent in Method A, it is true that it is impossible to avoid local supersaturation at the point of entry of the drop into solution and during its distribution in the volume of liquid as a whole. Therefore the method of homogenous precipitation is worthy of consideration. The conditions for this method are the presence of precipitant and the expected precipitate in one phase (in solution), and the precipitation occurs as the result of a slow reaction. Examples of homogenous precipitation are the well known nitride method of precipitating iron and aluminum, and also Willard's method of precipitating calcium oxalate [1] in which ammonia released by the hydrolysis of urea $CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3$, neutralizes the acid.

Because of the small concentration of the gas, this form of precipitant is very successful, because only slight supersaturation occurs. We shall consider this method below using the carbonization of aluminate solutions as an example.

Among other factors it is necessary to consider the effect of temperature on precipitates. Since the majority of precipitates have a positive temperature coefficient of solubility, heating increases the solubility, and usually the quality of the precipitate is thereby favorably affected. It is easy to see that the action of heat can also be unfavorable (decrease of solubility with temperature).

Vant-Hoff [4] in his study of borates established that it is easier to obtain them in a crystalline form in porcelain rather than in glass vessels; he also established that in a series of cases the introduction of seed(crystals) shows an effect only when a large amount of them are used. In such a case it is

necessary to introduce the concept of surface action.

Spiro [5] independently established and used the favorable action of large amount of precipitate for the formation of new lots of precipitate. He called this method the accumulation method, because the first portion of precipitate which is formed, is used as a nucleus for the formation of a second portion of precipitate; these two portions then act as nuclei for a third, etc., i.e. the precipitate gradually accumulates on the first crystals. We verified the effectiveness of this method [2]. It should be noted here that the method mentioned above -Method A- (the last drop method), obviously uses all the precipitate obtained as nuclei, as many times as new portions of precipitant (drops) are added, for the whole process. A mathematical treatment of this question[1] (A. V. Nikolaev) gave the following number of contacts of the seed crystals with the precipitation zone during the whole period of precipitate formation.

1) Drop Method B: $ma\,[\ln(m + 1) - 1]$.

2) Drop Method A (without seed crystals) $\frac{(m - 2)ma}{2}$

3) Drop Method A (with seed crystals): m^2a.

4) n-th successive precipitation: $nma\,\ln(m + 1) - ma$.

5) for n successive accumulations: $\frac{n^2}{2}\,ma\,\ln(m + 1) - nma$, where a is the number of crystals formed from one portion (drop); n is the number of precipitations; m is the number of drops (portions).

Comparison of drop methods A and B shows that A gives a $250\left(\frac{2}{1}\right) - 500\left(\frac{3}{1}\right)$ times more efficient use of the seed crystals than B. Comparison of the accumulation method [5] and Method A shows that one precipitation according to Method A is equivalent to 20-30 precipitations by Spiro's method.

Thus Method A is interesting not only as a means of lowering supersaturation but also as a very effective method of using seed crystals for further precipitation.[2]

In concluding this part of the work it is necessary to consider some simple ideas from the colloid field, which we shall use later on. Particles of precipitate can grow larger (or flocculate) at the expense of the true growth of the crystal and can " stick together" to coagulate. Ordinary coagulants (heat and coagulators) can therefore lead to an enlargement of the particle, although as known previously each increase in particle size does not necessarily lead to an improvement in the precipitate [1].

It is also obvious that a precipitant can also act as a peptizing agent for the precipitant with all the consequences that that entails (increase in the volume of the precipitate, a large final layer of deposit, etc.).

All the possible factors which can influence the quality of the precipitate, can act either with or against each other, e.g. in the majority of cases where heat is used, together with Method A, the effect of each factor is increased

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1) Only the final results are given due to economy of space.

2) We deem it a pleasant duty to record that Prof. N. A. Tananaev in his textbook of gravimetric analysis, proposed the method of pouring the two reactants into a buffer, before us. We arrived at this method independently of Tananaev's work and introduced some improvements - the use of seed crystals and the establishment of the minimum addition time.

separately. The method of homogenous precipitation usually matches with increase in precipitate solubility and with heating.

We have shown below by the use of four examples quoted previously, the effect of each of these factors, which enable us to define a more interesting field for further work. The filtration coefficient of the precipitate was taken as a criterion, i.e. the velocity in cm/sec of the movement of water in the precipitate for a gradient equal to unity.[1] The method of determination of the filtration coefficient has been described previously [2], accordingly it is not dealt with further. Only a diagram of the apparatus is adduced. (Fig.1). We obtained good reproducibility for the results as can be seen from the results of repeated determinations of the filtration coefficient K for three precipitates of $Fe(OH)_3$; I – 1.32; 1.14; 1.14; II – 1.7; 1.32; 1.32; III – 6.26; 6.34; 6.20. $K = 10^{-6}$ cm/sec.

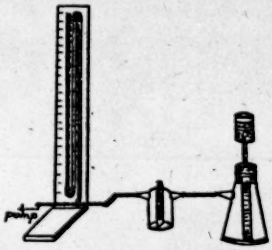

Fig. 1. Filtration apparatus

For I and II it was observed that the precipitate becomes gradually denser on the filter. It is not difficult to show theoretically that there is an inverse relation between the filtration coefficient and the square of the surface area of the precipitate particles (see e.g. [9]).

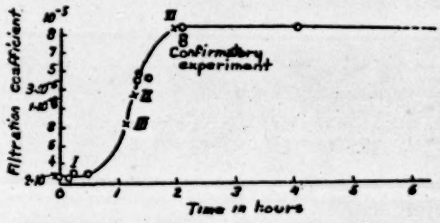

Fig. 2. Diagram of filtration of precipitates of $Mg(OH)_2$
×○– solutions of $MgSO_4$ and NaOH; ●– solutions $MgCl_2$ and $Ca(OH)_2$

We shall begin with Method B. The velocity of entry of precipitant drops can be greater than the velocity with which the drops are dispersed in the bulk of the solution. This leads to local supersaturation (from the meeting of the precipitation zone of the two drops) and to a depression of the growth of the particles. On decreasing the rate of addition a point is reached at which each drop will enter the solution just when the previous drop has been completely used up, the quality of the precipitate should then improve rapidly. Obviously further increases in the time of addition will not improve conditions much more than the critical rate. Results are given in Tables 1 and 2 below.

As can be seen from Table 1 and Fig. 2, our expectations were fully justified; for $Mg(OH)_2$ there are three groups and the increase in filtrability

[1] Just as useful as a qualitative numerical character of precipitate and deposit is its dynamics of settling and the depth of the final layer on standing. See below and also [2].

is stepwise. The addition time acts favorably on gypsum precipitates, but has considerably less effect on such colloidal and difficultly soluble precipitates as $Fe(OH)_3$ and $Al(OH)_3$. True, for a 4 hour addition in Series 3 the filtration coefficient increases by 2-3 times; but this, of course cannot be compared with $Mg(OH)_2$, where K increases 40-100 times.

The effect of increasing the temperature has been studied in detail for $Fe(OH)_3$ and $Al(OH)_3$, i.e., for precipitates on which addition time does not have much effect. Results are given in Table 2.

TABLE 1

Filtration Velocity of Precipitates (10^{-7} cm/sec) in Relation to Addition Time (precipitant dropwise)

No.	Precipitates	Addition time in hours						
		0.25	0.5	1	1.5	2.0	4.0	7.0
		Filtration coefficients						
1	$Mg(OH)_2$; 10% solutions $MgSO_4$ and NaOH	2.8	2.9	24.9	34.9	82-105	86-130	342
2	$Fe(OH)_3$; 5% solutions $FeCl_3$ and NaOH	11.8	15.0	-	14.0	11.6-13.2	-	-
3	$Fe(OH)_3$; 10% solutions $FeCl_3$ and NaOH	17.2	22.3	-	22.7	12-18.9	46.5-55	-
4	$Al(OH)_3$; 10% solutions $AlCl_3$ and NaOH	6-16.6	18.0	-	9.2-19.6	6.6-13.4	17.0	-
5	$Al(OH)_3$; 5% solutions $AlCl_3$ and NaOH	6	-	-	6.0	7.2	-	-
6	$CaSO_4 \cdot 2H_2O$; 10% solutions $CaCl_2$ and H_2SO_4	380-830	620-650	-	-	-	1300 - 1500 [1]	-

[1]) Addition time - 3 hours.

For addition times of less than 2 hours (1 drop/2 sec) the effect of temperature is not very significant for either $Al(OH)_3$, or for $Fe(OH)_3$ in particular (Compare with Table 1, Nos. 2 and 4). But since slow rates of addition are seldom used in practice, then it must be acknowledged that the action of heat alone is apparently exaggerated. This was unexpected, being contrary to general opinion, and so we repeated the experiments several times. Nevertheless, the results obtained were still the same. It is curious that heating has only a relatively small effect (increasing by 2-4 times) even for a 4-hour addition time (see No. 4, Table 1 and No. 3, Table 2); this is true also for a seven hour addition period.

Spiro's accumulation method which was tested for $Mg(OH)_2$ in particular, (see [2]) did not give better results even for 18 accumulations, than Method B for long addition times; this can be seen from Fig. 2, in which the Roman numerals represent the points for precipitates I-IX formed by accumulations. The accumulation method was therefore not used further.

The last drop Method A, obviously is effective only for a definite addition rate; thus, the precipitate of $Mg(OH)_2$ for an addition time of 15 minutes to the buffer cannot be filtered; for a 48-minute addition period $K = 7.5\text{-}11.0 \cdot 10^{-8}$ cm per second, and for a 2 hour addition period $K = 1.0 \cdot 10^{-5}$ cm/sec. No better results were obtained with this method than with Method B, but the advantages of Method A become apparent when $Ca(OH)_2$ is used instead of NaOH; it was only by means of Method A that a precipitate could be prepared with a $K = 10^{-5}$ cm/sec, when

$Ca(OH)_2$ was used as the precipitant. For $Al(OH)_3$, the precipitates obtained had a filtration coefficient of $8-9\cdot10^{-8}$ cm/sec for addition times of 1.5-3 hours, but these precipitates had one very important advantage - they settled out incomparably better than those obtained by Method B.

Table 2

Relation between Filtration Coefficients (K) of Precipitates (10^{-7} cm/sec) and the Addition Time at 80-90°C

No.	Precipitate	Addition Time in Hours					
		0.25	0.5	1.5	2.0	4.0	7.0
1	$Fe(OH)_3$; 5% solns. $FeCl_3$ and NaOH	12-19	-	13	13.4	1)	-
2	$Al(OH)_3$; 5% solns. $AlCl_3$ and NaOH (alkali to Al salt)	7.8	11.0	18.4	15.6	-	-
3	$Al(OH)_3$; 10% solns. $AlCl_3$ and NaOH (Al salt to alkali)	-	-	-	14.1-17.7	35-48	85-97

1) Long experiments in the precipitation of $Fe(OH)_3$ with heating give very badly filtering precipitates owing to changes in the precipitate.

$Fe(OH)_3$ precipitates obtained by Method A have a maximum filtration coefficient of $6.2\cdot10^{-6}$ cm/sec for a 2 hour addition time; these precipitates which settled out considerably better than precipitates obtained by other methods, were friable in appearance and did not smear glass.

By means of Method A precipitates of $CaSO_4$ were obtained for a 1 hour addition period with 96% H_2SO_4 as precipitant, which had record values for the filtration coefficient ($3.3-3.7\cdot10^{-4}$ cm/sec[2]). It is important to observe that even when 10% H_2SO_4 was used in Method B, the precipitates obtained did not have filtration coefficients better than $K = 5-6\cdot10^{-5}$ cm/sec. Thus Method A is very effective for some precipitates.

The method of homogenous precipitation was tested on $Fe(CH)_3$ (nitride method). The precipitate obtained had a $K = 3.5\cdot10^{-6}$ cm/sec, i.e. better than the normal iron precipitates, in addition it settled out very rapidly as can be seen from Table 3.

Only typical crystalline precipitates settled out as quickly.

In the carbonization of aluminate solutions we come across a case of the action of a gaseous precipitant. The result obtained was unique because in addition to a small supersaturation on addition of the precipitant, the solubility of the precipitate is comparatively good. The corresponding results are given in Table 4.

The significant effect of elevating the temperature is very curious in this case. The filtration coefficient was determined for a sample of factory produced $Al(OH)_3$ prepared by the centrifuge method (the precipitate was given to us by Prof. A. I. Lainder to whom we extend our thanks) and was found to be equal to $2.75\cdot10^{-4}$ cm/sec, i.e. somewhat worse than $Al(OH)_3$ obtained by the carbonization method.

2) In speed of filtration these precipitates are comparable with coarse grain sand.

Table 3

Settling Velocity of Precipitates of $Fe(OH)_3$; Obtained by the Nitride Method
(total layer: solid + liquid = 4.0 cm)

	Settling Time						
	10 min.	20 min.	30 min.	1 hour	2 hours	3 hours	3.5 hours
Precipitate layer in cm	0.8	0.75	0.75	0.75	0.75	0.75	0.75

NOTE: Final ratio $\frac{\text{solid}}{\text{liquid}} = 0.23$.

Results are given below which were obtained for $CaSO_4$ by means of Method B, and which illustrate the effect of the precipitant cation. In all cases 10% solutions of $CaCl_2$ were used, and 10% solutions of H_2SO_4, $MgSO_4$, Na_2SO_4, and K_2SO_4 used as precipitants.

Table 4

Carbonization of a 10% soln. in hours	Temp., °C	Filtration Coeff. K in cm/sec
4	Room	$8.7 \cdot 10^{-5}$
4	90-100	$3.0 \cdot 10^{-4}$
4	90-100	$6.0 \cdot 10^{-4}$

Record results were obtained for Na_2SO_4 and K_2SO_4.[1] These good results for instantaneous addition are apparently connected with the following interesting observations. After mixing in the course of a few tens of seconds, or often up to one minute, the solution obtained remained clear, and only at the end of that time did crystallization commence. The preparative process, which occurs in the supersaturated solution, apparently facilitates subsequent crystallization.

Table 5

Filtration Coefficients for $CaSO_4$ Precipitates
(10^{-7} cm/sec)

Precipitant (10% solutions)	Addition Time in Hours		
	instantaneously	1.0	3
H_2SO_4	680-1100	620-650	1300-1500
$MgSO_4$	520	440	1200
Na_2SO_4	2300	2000	2500
K_2SO_4	2100	3600	3100

The effect of coagulators was investigated for $Fe(OH)_3$ and $Al(OH)_3$, they were added so as to give a 5% solution. The concentration of the solution of iron and aluminum salts and the NaOH was also 5%.

It can be seen from Table 6 that coagulators increase the filtration coefficient of $Al(OH)_3$ by 4-15 times; on heating the solution, the sulfate coagulators give even higher results, but the action of chloride coagulators, in almost all cases, was unaffected by temperature and in some cases their action was even impaired. From Table 6 in particular it follows that in the analytical determination of aluminum, in order to improve the precipitate quality, it is better to precipitate the $Al(OH)_3$ in the presence of ammonium sulfate than the chloride which is the one usually used.

[1] The intermediate formation of fairly soluble double compounds of the type of glauberite or syngenite could be postulated here.

Ammonium chloride increased the filtration coefficient of $Fe(OH)_3$ in the cold 3-4 times, but Na_2SO_4 did not have any effect [contrast to $Al(OH)_3$]. On heating, both ammonium chloride and Na_2SO_4 increased the filtration coefficient. In this case, therefore, the use of ammonium chloride in the analytical precipitation of $Fe(OH)_3$ is justified.

Table 6

Filtration Coefficients of Precipitates (10^{-7} cm/sec) $Al(OH)_3$ and $Fe(OH)_3$ on addition of coagulators (5%)

Addition time [1 drop/2 sec]

Precipitate	Coagulators					Observations
	NaCl	NH_4Cl	$CaCl_2$	Na_2SO_4	$(NH_4)_2SO_4$	
$Al(OH)_3$	20-25	44.8	32.4	67.5-74.2	87.6	Ppt. obtained in the cold
$Al(OH)_3$	8.1	14.2	6.3	74-133	98.4	Ppt. obtained at 80°
$Fe(OH)_3$	12.1	54.3	9.5	13-20	-	Ppt. obtained in the cold
$Fe(OH)_3$	14.7	53.1	13.0	31.2	-	Ppt. obtained at 80°

Experiments were carried out on the precipitation of $Fe(OH)_3$ in which NH_3 and Na_2CO_3 were used instead of NaOH. [Rate of addition 1 drop/2 sec]. The filtration coefficient for NH_3 was $K = 1.77 \cdot 10^{-6}$ cm/sec while for Na_2CO_3 $K = 2.6 \cdot 10^{-6}$ cm/sec, whether the precipitation was carried out in the cold or at 70-80°, thus Na_2CO_3 gives a slightly better precipitate; it settles out quite well (see Table 10).

It is interesting that the substitution of $Ca(OH)_2$ for NaOH in the precipitation of $Mg(OH)_2$ gave an easily filterable precipitate only by the last drop Method A (1 drop/2 sec); but these precipitates settle out badly (particle adhesion).

The better filtrability of $Al(OH)_3$ and $Fe(OH)_3$ for the 10% series as compared with the 5% series is the result of a coagulating effect of this kind; the coagulant NaCl is formed during the reaction. Special experiments were made for $Mg(OH)_2$ in which 31.8% NaOH and 23% $MgSO_4$ were used, and in spite of a $1\frac{1}{2}$ hour addition time, the precipitate obtained had a $K = 8 \cdot 10^{-7}$ cm/sec (poor filtration). In this case the coagulating effect is negative and stops the true crystal growth. Thus N. A. Tananaev's rule is confirmed for $Fe(OH)_3$ and $Al(OH)_3$ but not for $Mg(OH)_2$.

When the colorimetric method of determining lithium is applied to natural brine with a 25-30% salt concentration the problem of separating magnesium as the hydroxide crops up. The application of Method A with $Ba(OH)_2$ as precipitant and the use of heat yields a precipitate with $K = 2.5\text{-}3.6 \cdot 10^{-6}$ cm/sec, which settles readily (see 8, Table 10). The coagulating effect here could not be completely suppressed which testifies to a definite limitation of Tananaev's rule.

The peptizing action of alkali together with a decrease in the solubility of hydroxide precipitates should become apparent when an inverse order of addition is used, e.g. adding a magnesium salt to alkali; in spite of a 2 hour addition time for 10% solutions the precipitate formed had a $K = 5 \cdot 10^{-7}$ cm/sec i.e. a twentieth of that for the normal method of addition. Consequently it is

to be expected that a lower result should be obtained for $Fe(OH)_3$ also. This was however, not confirmed experimentally, thus 5% solutions for a 2 hour addition time gave a precipitate for which $K = 1.32 \cdot 10^{-8}$ and 10% solutions gave precipitates with $K = 1.2$ and $1.9 \cdot 10^{-8}$ cm sec (compare Table 7).

Table 7

	Method B					Method A	Centri-fuging method	Carboni-zation of aluminate solutions
	Normal ppt.5% series	Same for 10% ser-ies	Increase in temp. during addition of 15% solution	Increase in conc. and addition time	Coagula-tors and increase in temp.			
$K = 10^{-4}$ cm/sec	0.6	1.7	1.1	9.7[1]	10.5-13.3	8-9	275	301-663[2]
Number of times increased	1.0	2.4	1.9	16	18-22	13-15	460	500-1000

[1] Inverse addition.
[2] At 90-100°, in the cold $K = 8.7 \cdot 10^{-5}$, i.e. increases 145 times.

On the addition of aluminum salts to alkali to form $Al(OH)_3$ a solution of aluminate is initially formed which is then decomposed by the aluminum salt according to the equation:

$$3NaAlO_2 + 6H_2O + AlCl_3 \longrightarrow 4Al(OH)_3 + 3NaCl$$

This decomposition period was extended to 4 and 7 hours. In this way the results of the third series given in Table 2 were obtained. As can be seen the precipitate formed was 30 to 50 times more difficult to filter than when decomposition of the aluminate was effected by CO_2, but about ten times easier than usual precipitates.

In concluding this section it is interesting to record results on the filtration coefficients of $Al(OH)_3$ prepared by different methods.

Without entering into a detailed discussion of this table, it can be said that the simple methods usually used (e.g. Tables 4,5 and 6) improve the filtrability of a precipitate (13-22 times) but increase of solubility and introduction of the reactants with minimum local supersaturation (gas) give a qualitatively different effect (an increase in filtration by 500-1000 times). On the basis of this method, therefore, it is necessary to get similar good results for other precipitates. The difference in the phase composition of the precipitates should be noted (for aluminates - other hydrated forms of Al_2O_3).

In confirmation of this we shall turn our attention to the fact that such a relatively soluble compound as $CaSO_4$ (0.22%), even for poor samples of precipitate has a $K = 3.8 \cdot 10^{-5}$ cm/sec[3] while good samples have a $K = 7.6 \cdot 10^{-4}$ cm/sec. For $CaSO_4$ the upper limit is the same as for $Al(OH)_3$, although the solubility of $Al(OH)_3$ in the usual media is small.[4] Apart from the good solubility of $CaSO_4$, the form of the crystals which has a definite significance, ensures loose packing on the filter.

[3] This value of K for $Mg(OH)_2$ is only attained for the best precipitates.
[4] In view of the final solution after carbonization.

Because of the extended form of the crystals of $CaSO_4$ the precipitates settle out rather poorly.

The use of the amphoteric nature of $Al(OH)_3$ gave exceptional results as mentioned above; the method cannot be used for $Fe(OH)_3$ and we did not succeed in getting any better results by Method A than a precipitate with $K = 6.2 \cdot 10^{-6}$ cm/sec.[1] It is interesting to try and find conditions for the precipitation of $Fe(OH)_3$ similar to those for $Al(OH)_3$. The best and worst precipitates of $Fe(OH)_3$ differ by 6-8 times in their filtrability.

Success was achieved for $Mg(OH)_3$ apparently because of its large solubility (solubility product for $Mg(OH)_2 = 10^{-10}$); therefore in conditions of low supersaturation (long addition time, by the use of Method A etc.) good precipitates with $K = 3 \cdot 10^{-5}$ cm/sec were obtained. Results are given for K for four precipitates. In concluding this section we shall deal with a few general questions. Let us consider first whether particles of the precipitate grow or stick together. We succeeded in showing in the case of $CaSO_4$ and $Mg(OH)_2$ the existence of "secondary" coagulation of the adhesion type [2]. This was the result of the large emmanating capacity of this type of precipitate [2] and the presence in the case of bad precipitates of coarser particles, when they were measured microscopically and by Figurovsky's method (sedimentation). But since precipitates with such "coarse" particles filter with difficulty, then it is natural to postulate an unstable adhesion of the particles, which the hydrostatic pressure during filtering can break down and thereby alter the form of the precipitate [2].

Table 8

Comparison of Filtration Coefficients for 4 Precipitates

Precipitate	$Mg(OH)_2$	$Fe(OH)_3$	$Al(OH)_3$	$CaSO_4 \cdot 2H_2O$
Solubility product or solubility in g/liter	10^{-10}	10^{-36}	10^{-38}	2.2
K_B Best ppts. in cm/sec	$3\text{-}4 \cdot 10^{-5}$	$6.2 \cdot 10^{-6}$	$7 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$
KW Worst ppts. in cm/sec	$2.8 \cdot 10^{-7}$	$8 \cdot 10^{-7}$	$6 \cdot 10^{-7}$	$3.8 \cdot 10^{-5}$
$\frac{K_B}{K_W}$	>100	~8	>1000	20

This secondary coarsening was shown experimentally. In Fig. 3 are given diagrams for the particle distribution of $Mg(OH)_2$ for a 20 minute and $1\frac{1}{2}$ hour precipitation; it can be seen that the badly filtering precipitate (20 minutes) has the coarser crystals. Then a four hour addition period was tried under the usual conditions with addition of up to 20% NaCl (coagulant). Determination of particle size in this case showed an even greater trail of coarse particles, undoubtedly because of secondary coarsening. The filtrability of the precipitate was depressed as was to be expected.

Consideration of Figs. 3 and 4 shows that good precipitates are surprisingly homogenous with regard to particle size distribution, thus for a 3-hour precipitation, 70% of the particles had radii of 6-8μ.[2] It is obvious that on improvement

[1] It is curious that precipitates of $Fe(OH)_3$ obtained by the homogenous precipitation method filter even slightly worse.

[2] In the theory of the water permeability of soils it is shown, that the presence of 10% of small particles determines the filtration of the soil (reason given by Mendeleev, see [7], p. 81.

the precipitates become even more homogenous, i.e. there is a limit in particle growth for given conditions of adhesion [2]. The existence of this limit is confirmed by the horizontal trend of the upper part of curve in Fig. 2 and also by sedimentation curves and X-ray photographs. X-ray photographs also show that precipitates consist of real and not ideal crystals. The presence of forking on X-ray photographs for the lines of good precipitates indicates that there are large internal stresses in the crystals because of irregular growth on the different faces. Block-crystallization is the reason for the limiting growth of particles during adhesion [2]. Block-crystallization also determines the trapping of mother liquor by the precipitate, and can anew explain the phenomena of coprecipitation and trapping (see below).

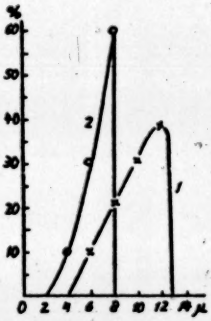

Fig. 3. Particle size distribution. Addition time: 1 - 20 min.; 2 - 1 hr. 30 min.

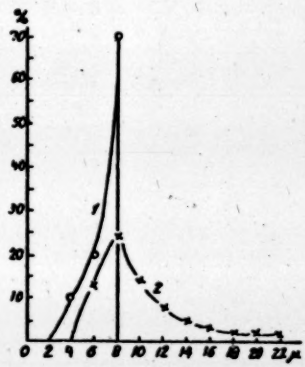

Fig. 4. Particle size distribution Addition time 3 hrs. 1) Without additiv ; 2) with addition of NaCl.

In addition to the particle size, their emmanating capacity and the differences in the X-ray photographs of precipitates with different filtration coefficients, precipitates also differ in other respects. The heating and dehydration of precipitates of $Mg(OH)_2$ corresponding to the lower and upper parts of the curve in Fig. 2 are represented in Figs. 5 and 6. From Fig. 5 it can be seen that the cessation of boiling (decomposition of the hydroxide) for small precipitates can be 25° low r than for coarse precipitates. These two curves reproduce experimentally two types of brucite [the natural form of $Mg(OH)_2$], discovered earlier [8]. Thus conditions similar to those employed by us are also met in nature.

The break on the heating curve in the case considered corresponds to boiling, or more exactly, to the dissocation tension equal to 1 atmosphere. [$Mg(OH)_2 \longrightarrow MgO + H_2O$] It is obvious that dehydration under isothermal conditions should differ considerably; this is shown with great clarity in Fig. 6: where I is the precipitate containing small crystals which have been dehydrated in the course of a few days; VI and IX are precipitates (similar to the 2-hour one) which lose a similar amount of water only after 40 days and this at a temperature of 250°, and under exactly the same conditions (the same oven, the same weights and crucibles, etc.).

Some results for the washability of precipitates are given below. Precipitates of $Mg(OH)_2$ formed after 9 accumulations by Spiro's method and washed until no reaction for SO_4^{2-} was given by the wash liquors contained the following amounts of SO_4^{2-} in the precipitate (Table 9).

In a repeat of the 9 accumulations the last precipitate contained 0.25% SO_4^{2-}. A precipitate obtained by Method A for a 2 hour precipitation time (the best precipitate for filtrability) contained 0.40% SO_4^{2-}, while a precipitate obtained by inverse addition (worse precipitate for filtration) contained 0.13% SO_4. Factory precipitates of $Al(OH)_3$ are known to contain an appreciable amount of sodium which has not been washed out, with a consequent bad effect on the quality of metallic aluminum. It is also known from factory practice that when precipitates contain coarse crystals it is difficult to get a very pure product. Therefore in the preparation of analytical precipitates it follows that they can be obtained in an easily filterable state only by separation from the main bulk of the contaminating ions of the mother liquor, but precipitation of easily filterable precipitates before calcining, apparently cannot be recommended.

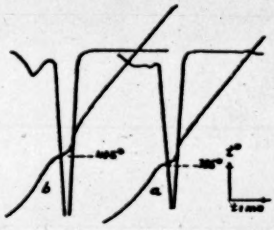

Fig. 5. Thermogram of $Mg(OH)_2$ ppts. Recording of both thermograms was made on one sheet of photographic paper.

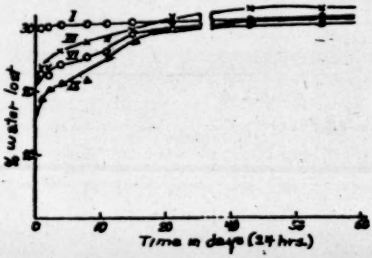

Fig. 6. Dehydration of precipitates of $Mg(OH)_2$ at 250°
Precipitates I–IX precipitated by the accumulation method

It is interesting that the usual adsorption mechanism for entrapping is not so responsible for the contamination of precipitates as is usually accepted. Thus, a precipitate which filters badly (I, Table 9) showed least contamination.

The curves for the settling rates of precipitates in general behave similarily to the filtration coefficient, as can be seen from Fig. 7 for $Mg(OH)_2$ precipitates. From curves 2-6 Fig. 7, the approach to a definite value is clearly shown both by the filtration coefficient, and the determination of particle size of the precipitates (see above). A case where the filtration coefficient did not correspond to the settling rate of the same precipitate was observed earlier, and is connected with unstable adhesion of the particles.

A very interesting phenomenon was observed during the precipitation of $Al(OH)_3$ and $Fe(OH)_3$ in 5 and 10% solutions. After addition of approximately 70-80% of the precipitant, all the contents of the vessel transformed into a fairly thick gel, that often stopped the stirrer. However, on further dilution of the alkali, the gel thinned out and at the equivalent point gelatinization ceased. The presence of developing space links between the particles is manifested in a very interesting type of settling out. Initially there is no settling out at all (10-40 minutes), but then a very sudden and rapid onset of settling out commences.

Gelatinization was never observed with precipitates prepared by Method A, which indicates that the surface forces of the particles of this type of precipitate are saturated, e.g. $Fe(OH)_3$ obtained by this method, did not smear glass and was friable.

Finally Table 10 gives the values of the final settled out layer in cm for a total layer of 4 cm after mixing. All the results are for 10% solutions.

Table 9

No. Precipitates	I	III	IV	IX
% SO_4^{2-} in precipitates	0.05	0.15	0.14	0.17

NOTE. Since this is essentially a one accumulation precipitate, then obviously, the mechanism of intercrystalline entrapment acts.

Results for precipitates for which the final settling layer is attained in 10-15 minutes or less are given in square brackets; in the dotted square brackets results are given for precipitates, in which settling out finished in 20-30 minutes.

The amphoteric character of precipitates of $Fe(OH)_3$ is shown by the fact that the precipitates are friable. Packing of precipitates may be effected by use of Method A, by precipitation with Na_2CO_3, by the addition of a coagulant and especially by the homogenous precipitation method. In the last case packing of the precipitate was the same as for the remaining three precipitates which could almost never be prepared in an amorphous condition as estimated by X-ray photographs.

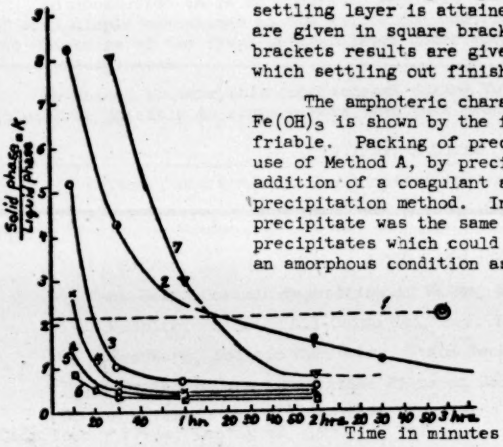

Fig. 7. Settling out of $Mg(OH)_2$ precipitates. Time of NaOH addition: 1 - 0.25 hr; 2 - 0.5 hr; 3 - 1 hr; 4 - 2 hrs.; 5 - 4 hrs.; 6 - 7 hrs.; 7 - confirmatory expt. (2 hrs)

For Method B packing was equal for $Mg(OH)_2$ and $Al(OH)_3$. For an inverse method of addition, the precipitates of $Mg(OH)_2$ and $Fe(OH)_3$ showed a breaking up from the OH-ion ; while for $Al(OH)_3$ the precipitate obtained was denser in complete agreement with its amphoteric character.

TABLE 10

Time and Method of Preparing Precipitates

Precipitate	Method B: time in hours				Reverse drop 2 hours	Method A without heating	Method A with heating	Nitride method	Carbonization of aluminate	Method B Na_2CO_3 precipitant	Method B Coagulant Na_2SO_4 with heating
	0.25	0.5	1.5	2							
$Mg(OH)_2$	1.8	1.5	1.2-1.3	1.2 (0.9[1])	3.3	1.4	1.0	–	–	–	–
$CaSO_4 \cdot 2H_2O$	3.3	–	0.75	0.7	–	0.7	0.7	–	–	–	–
$Al(OH)_3$	1.0	1.35-1.5	1.05	1.25	0.6	1.0	0.7	–	0.7	–	–
$Fe(OH)_3$	3.6	3.45	3.4	3.15	3.45	3.1	1.16	0.75	–	1.7	1.45

[1]) For 4-hour addition.

The best settling out was observed for $Mg(OH)_2$ for a 7-hour addition time by Method B, and by Method A with heating.

It is interesting that a layer less than 0.6-0.7 cm was not obtained for any precipitate (10% of the solution).

In conclusion it is necessary to emphasize once again that the measurement of such simple magnitudes as the filtration coefficient, the settling velocity, and thickness of the final settled layer gives very important and useful results about precipitates.

We intend to take this into account during further investigations, in which it will be possible to compare more than four precipitates.

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COMPLEX COMPOUNDS AND THEIR APPLICATION IN ANALYTICAL CHEMISTRY[1)]

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For some time past in connection with increasing attention to control, particularly of new processes, the scope of investigations in analytical chemistry has not only widened, but the character of the investigations themselves has changed. This is reflected in attempts to depart from empirical and semi-empirical analytical methods and to work out methods which are based firmly on the basic principles of inorganic and physical chemistry.

In analytical chemistry the very attractive theory exists that it is possible to find ways of independently determining chemical elements in the presence of others. The new problem of determining and controlling so called traces and mixtures on the background of an excess of the main elements has arisen.

The development of methods for isolation, separation and estimation of many rare and widely scattered elements has become an independent problem.

Progress in analytical chemistry to a considerable degree develops along the path of the widest use in analytical chemistry of such instrumental methods of analysis as the photocolorimetric, electroanalytical, polarographic, spectrographic, X-ray, mass spectrographic, chromatographic, luminescent, and radiochemical methods, as well as the use of radioactive isotopes.

The use of instruments in analytical chemistry does not lessen, but in fact increases the tempo of investigation of chemical reaction in solutions.

If under these conditions the classical methods of analytical chemistry begin partly to loose their independent significance, on the other hand the accumulation of a vast amount of experiments on the relation of the chemical affinity of analytical processes constitutes a basis for the instrumental methods, the successful use of which often depends on the extent of the identification of the material to be determined.

In order to solve new problems in analytical chemistry both here and abroad more and more investigations are being carried out on the discovery and use of special organic compounds for use as precipitants, pigments and indicators. Many organic reagents are already firmly established in practical analysis because of the high intensity of the colors of the compounds formed and the low solubility of the precipitates.

The problems of analytical chemistry which are of practical importance can be successfully solved by a more fundamental approach to the chemical side of analytical processes by a more complete use of the fine structure of molecules created by the analyst.

Nevertheless in analytical chemistry there is still a definite neglect of the chemical side of processes, particularly in the more complicated cases connected with complex formation. If, as a rule, in all analytical processes the valency state of an element is taken into account, the coordination number of the instab-

[1)] Report read at the Conference on Classical Methods of Chemical Analysis, held in Moscow on November 14-17, 1951.

ility constants for many elements still remain unknown, and deliberate control of the chemical affinity of an analytical process is impossible without knowledge of the coordination possibilities, the dimensions of the ionic radii and charges, and the capacity of individual groups and molecular residues for complex formation.

Platinum and to a lesser degree some of the elements in the same group, is the only metal whose stereochemistry has been more or less studied in detail. The complex compounds of the majority of the other elements have either been studied unsystematically and superficially or have not been studied at all. It is sufficient to remember that the stereochemistry of such an ancient element as gold is still little known, to say nothing of many rare and scattered elements. The physical chemistry of even known complex compounds is in an even more unsatisfactory state. There are no conclusive experimental results on the instability of many complex compounds of importance in analytical chemistry, in aqueous solution in relation to pH and other factors. Numerical values of the instability constants of complex compounds of different elements are no less necessary for analytical chemistry today than the solubility product values. Thermal stability, decomposition potential, the phenomena of oxidation and reduction of complex compounds, and others have still not found wide application in analytical chemistry.

On examination of textbooks and specialist literature it is easy to be convinced that the formation of complex compounds is very widely used in analytical chemistry.

From the time of the discovery by Ilinsky of the reaction of Co with α-nitroso-β-naphthol [1] and afterwards of Ni and Pa with dimethylglyoxime by Chugaev [2], inner complex compounds have been widely used in practical analytical chemistry. Hydroxyquinone, rubeanic acid, thiourea, diethylthiocarbamate, diphenylthiocarbzone, and many other organic reagents, specially synthesized for analytical purposes, have often been applied in colorimetry for preparing colored complexes and for the precipitation of the elements.

Information on inner complex compounds of interest in analytical chemistry is given in Voznesensky's book [3]. Kuznetsov [4] has carried out systematic study in this field.

It must be noted that the study of the reactions of organic reagents, unfortunately is still of a predominantly qualitative nature. We often do not know even the composition of the reaction products and the chemical affinity of the process of formation and decompcsition of intracomplex compounds.

Inner-complex compounds are of special interest for analytical chemistry and should be considered independently. Below we give examples of the application of some special complexes in analytical chemistry.

Of great importance in analytical practice are phenomena such as the so-called "masking", whereby with the help of complex forming compounds interference from similar elements can be eliminated. Thus the determination of rhodium in platinum-rhodium alloys (contact, thermopar) is exceptionally difficult. It has been shown that both metals behave differently towards sulfites [5]. Pt after dissolving in aqua regia, in aqueous solution is in the form of $[PtCl_6]^{2-}$ which is of an orenge color while Rh as $[RhCl_6]^{3-}$ gives an intense rose color. On addition of Na_2SO_3 to the mixture the sulfite reacts only with Pt forming a completely colorless complex sulfite compound of the composition $Na_6[Pt(SO_3)_4]$. Rh remains unchanged and can be determined from the characteristic color of the chlororhodiate.

A small number of rare earth elements and Ca can be separated from Fe, by the addition of NH_4F to the solution which is being analyzed. Fe forms a stable soluble complex of the composition $(NH_4)_3[FeF_6]$, while the rare earths and Ca are

precipitated as fluorides.

Fe ions are bound into a stable complex by the addition of citrate, tartrate, phosphate, pyrophosphate etc., to form anions of the composition $[Fe(Cit)_2]^{3-}$, $[Fe(Tar)_3]^{3-}$, $[Fe(PO_4)_3]^{3-}$, $[Fe_2(P_2O_7)_3]^{6-}$ [6]. Fe cannot be detected in solutions containing such complex compounds even with the most sensitive reagents.

Zr can be transformed into a very stable citrate complex of the composition $H_4[ZrF_2Cit_2]$ in the determination of small amounts P in metallic Zr by ammonium molybdate.

In order to avoid interference from Fe, Ni, Co in the determination of Cu by rubeanic acid, citric acid is added [7]. The interfering metals are combined into very stable complex anions of the composition $[Me(Cit)_2]^{4-}$, while Cu in these conditions is reduced to the univalent state and yields a difficultly soluble rubeanate.

In the separation of heavy metals, bivalent Cu can be masked by addition of thiosulfate. The univalent Cu thus formed gives a colorless, stable complex compound of the composition $Na_3[Cu(S_2O_3)_2]$ [8].

During the separation of Al from solution by means of hydroxyquinoline in the presence of PO_4^{3-}, tartaric acid and NH_3 are first added in order to combine with Al to form a complex anion $[Al(Tar)_3]^{3-}$ [9] which is stable in alkaline media.

For elements which are similar to each other in chemical properties, the differences in the stability of complexes of the same kind may be used for separating them to a greater extent than is done at present. Sometimes it is possible to vary the stability of the complex compounds within wide limits. By increasing the acidity e.g. by addition of HNO_3 or H_2SO_4, as a rule, the coordination links of the central atom with the residues can be weakened particularly if the latter are anions of weak acids. HCl and acetic acid are not so suitable for acidification, because their anions form complexes with the metal ions.

On the other hand alkalization sometimes strongly consolidates the complex. Very indicative in this connection are the complex citrates of the rare earth elements of composition $Na_3[Me^{III}(Cit)_2]$ which in acid solutions dissociate practically completely according to the equation

$$Na_3[Me^{III}(Cit)_2] \rightleftharpoons 3Na^+ + Me^{3+} + 2Cit^{3-}.$$

By the addition of NH_3 initially to the neutral solution the citrate complexes are strengthened to such an extent, that the ions of the rare earth elements cannot be precipitated by oxalate or fluoride ions [10].

On acidification of the complex anion $[Fe(CN)_6]^{4-}$, its inner sphere dissociation increases. The simple ions Fe^{2+} thus formed then react with ferrocyanide ions to give blue colored compounds.

Dimethylglyoxime is an equally good reagent for both bivalent Pt and Pd ions. These elements yield complex compounds with $NaNO_2$ which differ appreciably in stability. The instability coefficients of $Na_2[Pt(NO_2)_4]$ is very small and enables Pd to be precipitated by addition of an alcoholic solution of dimethylglyoxime, from a mixture of Pd and Pt after a preliminary nitrite treatment.

In the colorimetric determination of Co with nitroso-R-salt, the elimination of interference from a number of heavy metals (Fe, Ni, Cu, Cr, etc.) is of vital importance, since some of them give colored complexes similar to Co (viz Fe, Cu,Ni)

while Cu and Ni ions are colored themselves. However, because of the difference in stability of the complex compounds formed, on acidification with HNO_3 only the colored compound of Co with nitroso-R-salt persists [11].

In the determination of small amounts of Co present in large amounts of Fe, Ni and Cu, the latter are removed by boiling with excess sodium acetate. Co remains in solution in the form of a stable acetate complex $Na_3[Co(CH_3COO)_6]$. The acetate complexes of Fe, Ni and Cu decompose with separation of $Fe(OH)_3$, $Ni(OH)_2$, and CuO respectively [12].

A method of separating Co in the form of the difficultly soluble compound $Ag_3[Co(CN)_6]$ is based on the different stabilities of the cyanide complex compounds $K_3[Co(CN)_6]$ and $K_4[Ni(CN)_6]$ in acid solution, Ni remains in solution in the form of the simple cation [13].

For the same reason during electrolysis of solutions of the cyanide complexes of Co and Ni, only the latter yields a black precipitate of NiO on the anode.

Os and Ru with excess thiourea form red and blue colored complexes respectively [25]. In order to detect Os in the presence of Ru therefore an excess of diethyldithiophosphoric acid is added to the thiourea complex of these elements; the less stable Ru complex is decomposed. If Os is present, then the solution will be colored the rose or red color of the thiourea complex of Os [45].

Mo always turns up in the colorimetric determination of Re. Both these elements give colored complexes with thiocyanates of the probable composition $K[MoO(CNS)_4]$ and $K[ReO(CNS)_4]$. On strong acidification, only the Re complex remains because of its greater stability [15]. In this case the choice of acid is very important, HCl will not only change the acidity of the medium, but excess of Cl ions is sufficiently strong to act as coordination substitutes and can lead to a change in the composition of the thiocyanate complex of Mo.

In this connection it should be observed that the analyst often has to deal with complex solutions in which different anions exist together with metallic cations. Under such conditions complex formation in the solution must be considered. Different acid radicals and neutral molecules show different tendencies to complex formation with metal ions. The following empirical series was found for bivalent Pt [16, 17]:

$$CN^- > S_2O_3^{2-} > I^- > SCN_2H_4 > SCN^- > NO_2^- > Br^- > C_5H_5N > Cl^- > OH^- > SO_4^{2-},$$
$$NO_3^-, ClO_4^-.$$

In this series tendency to complex formation decreases from left to right. Bivalent Pt forms complexes with the most reactive of these coordination substituents in solution. Similar series could be established for the ions of other metals.

Many difficultly soluble complex compounds give crystals of very characteristic form, which are suitable for identification of the elements. In Korenman's book [18] a fairly large number of such examples are given.

The complex chromooxalate of K, $K_3[Cr(C_2O_4)_3]$ forms characteristic precipitates in the form of green rhomboids under the microscope, only with the first four elements of the rare earth group, the composition is $Me^{III}[Cr(C_2O_4)_3]$, where Me^{III} is La, Ce, Pr, Nd [19]. The majority of other elements do not interfere.

For detecting SO_4^{2-} successfully the thiourea complex of Pt can be used

$[Pt(Thio)_4]Cl_2$. In the presence of SO_4, a very characteristic crystalline precipitate of composition $[Pt(Thio)_4]SO_4$ separates out instantly. Other anions containing S, SO_3^{2-}, $S_2O_3^{2-}$ do not interfere, because they form precipitates different in form and composition, such as $[Pt(Thio)_3SO_3]$ and $[Pt(Thio)_3S_2O_3]_3$ [20].

The formation of difficultly soluble complex compounds could be of far greater significance in gravimetric analysis. In the majority of cases the crystalline precipitates formed do not trap impurities, which is a very characteristic property of bulky precipitates.

The classical method of determining K by means of sodium chloroplatinite is based on the fact that the solubility of the complexes of composition $Me_2^1[PtCl_6]$ where Me = Na, K, Rb, Cs decreases rapidly with the increasing atomic weight of the cation. Such regularities are found in other cases. Thus silicomolybdic acid $H_8[SiMo_2O_7]_6$ gives crystalline, difficultly soluble precipitates with salts of Rb and particularly Cs.

The solubility of complexes of the type $Me_2^1[SnCl_6]$ essentially changes from Li to Cs.

In the reaction of $(NH_4)_2[Hg(CNS)_4]$ with Cu^{2+}, Ag^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, precipitates are formed which differ in solubility, are similar in the constitution of the outer sphere and of the type $Cu[Hg(CNS)_4]$ or the mixed type $(NH_4)_2Co[Hg(CNS)_4]_2$.

Substitution in the outer sphere of K in the cyanide complexes of Fe, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$, for heavy metal ions leads to formation of difficultly soluble compounds [21].

Of interest is the systematic study of the formation of difficultly soluble compounds; thiocyanates, cyanides, sulfites, oxalates and other complexes.

It is possible to prepare difficultly soluble complexes by substitution in the outer sphere of the complex cations $[Co(NH_3)_6]^{3+}$ $[Cr(NH_3)_6]^{3+}$, $[Cu\ en_2]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Cd(NH_3)_4]^{2+}$ and others with the chlorate radical to give e.g. $[Cd(NH_3)_4](ClO_4)_2$ [22].

Anions of organic sulfonic acid also form difficultly soluble compounds, in which the solubility decreases with complexity of the hydrocarbon skeleton of the sulfonic acid $[Cr(NH_3)_6]$ $(C_7H_6NSO_3)_3$; $[Cr(NH_3)_6]$ $(C_{12}H_6N_2SO_3)_3$; $[Cr(NH_3)_6](C_{14}H_7O_4SO_3)_3$.

Practically insoluble complexes can be prepared by combining complex cations and anions, e.g. Magnus' green salt $[Pt(NH_3)_4]$ $[PtCl_4]$.

By the interaction of antipyrine or pyramidone with ions of many of the heavy metals, complex cations are formed of the general composition $[Me(C_{11}H_{12}ON_2)_6]^{2+}$ with high molecular weights.

Complex ammoniate groups can be used as complex cations in precipitation reactions e.g. $[Cu(NH_3)_4]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Ni(NH_3)_6]^{2+}$ and other nitrogen derivatives such as $[CdPy_4]^{2+}$, $[ZnPy_4]^{2+}$, $[HgPy_4]^{2+}$ and $[NiPy_6]^{2+}$.

In a number of cases the formation of multi-complexes finds an application in analytical chemistry.

By the action of $[Co(NH_3)_6](NO_3)_2$ on a mixture of the complex fluorides of Be, Mg, Al, Zn and Sc, a precipitate containing only the complex fluoride of Sc can be formed $[Co(NH_3)_6][ScF_6]$ [23].

The slightly stable complex of univalent Cu, $H[CuCl_2]$ forms a difficultly soluble precipitate of the composition $[Pt(NH_3)_4][CuCl_2]_2$ [24].

The formation of multi-complexes of the type $[Me^{III}(C_{11}H_{12}ON_2)_6][Cr(CNS)_6]$ with a very high molecular weight by the action of phenyldimethylpyrazolone on the rare earth elements and a number of other metals is worthy of the analyst's attention [26].

Practically insoluble complex compounds can be obtained in many cases by substitution in the outer spheres of organic cations of the ammonia type, e.g. pyridine (PyH^+), quinoline (XyH^+), antipyrine ($AntH^+$), etc. Such complexes are $(C_5H_5NH)[AuBr_4]$, $(C_9H_7ONH)K_3[Fe(CN)_6]$, $(C_5H_5NH)_2[HgI_4]$, $(C_9H_7ONH)[BiI_4]$ and $(C_{11}H_{12}ON_2H)[HgI_4]$, etc. Gusev used many compounds of a similar type for analytical purposes [27].

Complex compounds of the non-electrolyte type are of special interest in analytical chemistry. Such compounds are easily formed by metals of the Pt group, particularly Pt and Pd, e.g. platinum diammine dichloride $[Pt(NH_3)_2Cl_2]$. $[Pt(Thio)_2Cl_2]$ [28], $[Pt(NH_3)_3S_2O_3]$, $[Pt(Thio)_3S_2O_3]$ and $[Pt(NH_3)_3SO_3]$ are also only very slightly soluble [29].

Similar types of practically insoluble crystalline compounds can be obtained for other metals, e.g. $[Hg(Py)_2Cl_2]$, $[Cd(Py)_2Cl_2]$, $[Pb(Thio)_2Cl_2]$, $[Cu(Py)_2(CNS)_2]$ and $[Ni(Py)_2(CNS)_2]$.

Pb can be separated from Bi by precipitating the Pb with excess thiourea to give a crystalline compound which is practically insoluble and has the probable composition $[Pb(Thio)_2(NO_3)_2]$. Bi remains in solution in the form of a complex compound of the composition $[Bi(Thio)_4](NO_3)_3$ [30].

From a solution containing Cu and Ni, pyridine precipitates Ni in the form $[Ni(Py)_3Cl_3]$ while Cu remains in solution as $[Cu(Py)_4]Cl_2$.

The complex compound of Hg, $K_2[HgI_4]$ reacts differently with pyridine and the pyridine ion, forming difficultly soluble complexes. In the first case the compound formed is $[Hg(Py)_2I_2]$ and in the second $(PyH)_2[HgI_4]$. The compound $[Hg(Py)_2I_2]$ on heating, dissolves and is transformed into $[Hg(Py)_4]I_2$, but on cooling it separates out in the unchanged form again.

Complex compounds are of exceptional importance in chromatographic analysis.

The synthetic resins (SBS, Espatite-1, KU-2, Amberlite, Dowex, Wofatit, etc.) are products of the polymerization of styrene, and the condensation products of phenol and formaldehyde and their derivatives. As a result of special treatment active groups are introduced into their molecules, e.g. $R\text{-}SO_3$, R-COOH, R-OH in the nucleus or side chain. Since the active groups are connected with the skeleton of the resin, they cannot transfer into solution. Only the H ion or cations which have replaced it retain their mobility ($R\text{-}SO_3H$). In this sense the solid phase of the resin represents a strongly dissociated acid or its salt.

The general reaction of ion exchange can be expressed by the equation:

$$\underline{n}\ R\text{-}SO_3H + Me^{n+} \rightleftarrows (R\text{-}SO_3)_nMe + \underline{n}H^+$$

where Me = Na, K, Ca, Mg, Al, Fe.

Ion exchange reactions can be considered as heterogeneous processes between active groups of the resin in a gel phase and the external phase of the solution, which proceed according to the law of mass action.

In the analysis of natural materials and different alloys, the problem can be reduced to a choice of a suitable complex compound former which can form a

complex anion with one of the elements to be determined. The separation of Fe and Al or Fe and Mg is based on the fact that Fe ions being good complex formers with many acid radicals can form complex anions. Even in HCl solutions, Fe exists as $[FeCl_6]^{3-}$ while Al and Mg remain as the simple hydrated cations Al^{3+} and Mg^{2+}. When a solution containing these three elements is passed through a column packed with a cation exchange resin (cationite) in the hydrogen form, Al and Mg are retained on the active groups of the resin; while the complex Fe ion passes through the column unchanged.

$$3R\text{-}SO_3H + Al^{3+} \longrightarrow (R\text{-}SO_3)_3Al + 3H^+.$$

The chromatographic separation of Fe and Cu is a more complicated case. Both these metals are good complex formers. Therefore, in HCl solution both metals are present in the form of complex ions $[FeCl_6]^{3-}$ and $[CuCl_4]^{2-}$, nevertheless separation can still be effected. In the analysis of a bronze ligature, sodium pyrophosphate was chosen [31]; this reacts with Fe and Cu to form complex anions of the composition $[Fe_2(P_2O_7)_3]^{6-}$ and $[CuP_2O_7]^{2-}$. The Cu complex is considerably less stable and on treatment with NH_3 solution it is converted into the complex cation $[Cu(NH_3)_4]^{2+}$. When the mixture thus treated is passed through a column containing a cationite the Fe complex is completely separated from Cu and passes through the column in the form of the complex anion, while the Cu complex cation is retained by the active group of the resin.

$$2R\text{-}SO_3H + [Cu(NH_3)_4]^{2+} \longrightarrow (R\text{-}SO_3)_2[Cu(NH_3)_4] + 2H^+.$$

A mixture of Fe, Al and Cu can be successfully separated by the use of the unequal stability of their citrate complexes. On addition of NH_3 only Fe and Al are transformed into the complex anions $[Fe(Cit)_2]^{3-}$ and $[Al(Cit)_2]^{3-}$, Cu in this case forms the complex cation $[Cu(NH_3)_4]^{2+}$. When the solution is passed through a cationite column, the Fe and Al pass through into the filtrate. The filtrate is then acidified to a pH 1.5 to 2, when the less stable Al anion decomposes and Al is precipitated as the single cation Al^{3+}. A second passage of the solution through the cationite column leads to separation of Fe from Al.

The analysis of ore slime Pt is considerably simplified since on separation from the original solution of the excess HCl, the noble metals appear as complex anions, $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$, etc., while the other, non-noble metals, will be in the form of simple cations Fe^{3+}, Cu^{2+}, Ni^{2+} [32]. After prolonged heating of the HCl solution of the Pt group metals, Ru in the form of a simple cation is completely retained by a cationite while the other elements of this group go into the filtrate in the form of complex ions.

The chromatographic separation of such closely related pairs of elements as Co and Ni can be effected by oxidation to the trivalent state whereby Co is converted into a stable anion while Ni for a sufficient acidity of the solution remains as the simple cation.

By the use of a cationite in combination with radioactive indicators, it is possible to separate elements which resemble each other very closely in chemical properties, such as the alkaline earths or rare earth elements [33]. In the latter case the metals which are retained on the upper part of the column are washed with a solution of complex formers at a definite pH. The problem of separation in this case reduces to finding the range of acidity of the solution produced by organic acids (citric, tartaric, oxalic, etc.) at which a difference can be detected in the instability constants of the complexes of the pairs of elements to be determined [35]. In its progress along the column during washing, the element with the most stable complex anion moves fastest into the filtrate.

Hitherto mention has been made of only a few separations in analytical mixtures effected by means of cation exchange. In some cases anion exchange resins (anionites) can be used for this purpose, but owing to their lower stability to acid and alkalis, this form of synthetic resin is not quite so suitable for analytical purposes as the cationites.

It is of great importance in analytical chemistry that the component parts of the complex (the nucleus and the coordination groups) suffer essential changes as a result of complex formation. It is useful to consider a few examples.

The dioxime forming part of Pd dioxime is easily oxidized to products of complete combustion, while dioxime on its own is oxidized only to intermediate compounds [36].

Oxalic acid titrates with $KBrO_3$ in HCl solution only very slowly and incompletely. The oxalate groups and bioxalate in Pt complexes are just as easily oxidized as with $KMnO_4$ [37].

Aminosulfonic acid even at high temperatures cannot be oxidized by $KMnO_4$ but as a component of the complex $[Pt(NH_3)_2(NH_2SO_3)Cl]$, it is oxidized just as easily as free oxalic acid [38].

Many metallic ions which are components of complex ions are oxidized appreciably more vigorously than when in the form of a simple ion, e.g. $[Ce^{III}(Cit)_2]^3 \longrightarrow [Ce^{IV}(Cit)_2X_2]^{4-}$, $[Co^{II}(NO_2)_6]^{4-} \longrightarrow [Co^{III}(NO_2)_6]^{3-}$, $[Cu^{I}(NH_3)_2]^{+} \longrightarrow [Cu^{II}(NH_3)_4]^{2+}$.

Weak boric acid in the presence of certain organic compounds can be titrated with phenophthalein as a unibasic acid [39].

Thiosulfuric acid does not exist in the free state, and thiosulfates slowly decompose in acid media. Coordinately bound thiosulfate radicals are stable towards acid, and the complex acid of composition $H_2[Pt(S_2O_3)_4]$ is as strong as H_2SO_4 [40].

During the formation of complex compounds the oxidation-reduction properties of the system change considerably, an important consideration for analytical purposes.

The value of the potential of a complex oxidation-reduction system is determined by the relations of the concentration of ions of oxidizer and reducer not bound up in the complex form. The concentration of single ions in its turn is determined by the instability constants of the complex compound formed, and depends on the concentration of complex forming compounds.

Thus for the systems Fe^{3+}-Fe^{2+} a decrease in the oxidation-reduction potential in H_2SO_4 is observed for the most reactive complex forming compound in the following order H_3PO_4 (0.516 V); $H_2C_2O_4$ (0.462 V); HF (0.422 V); $H_4P_2O_7$ (0.416 V).

For the system VO^{2+}-V^{3+} in H_2SO_4 when phosphoric acid, ammonium fluoride are used as complex formers, it is possible to get solutions with potential values in the range 0.621 to 0.279 V [41].

The constituents of complex compounds are susceptible in a series of cases to successive oxidation. Thus in the compounds $[Pt(NH_3)_4]$, $[Pt(CN)_4]$, Pt in the complex cation and anion is oxidized separately, and is expressed on the potentiometric titration curve by two steps for different potential values [42]. In the Pt-bioxalate of composition $[Pt(NH_3)_2(HC_2O_4)_2]$ the bioxalate group and the Pt are titrable in a definite order; first the Pt and then the bioxalate

groups successively [43]. In the thiosulfatoplatinite complex $K_2[Pt(NH_3)_2(S_2O_3)_2]$ on oxidation with bromate the following order is observed. $S^{2-} \rightarrow S^0$ (1 step), $Pt^{2+} \rightarrow Pt^{4+}$ (2 steps) and $S^0 \rightarrow S^{6+}$ (3 steps) [44].

The examples quoted here by no means exhaust all the multitude of possibilities of applying complex compounds in analytical chemistry.

In conclusion we would like to express the hope that there will be a considerable expansion in the number of investigations in the application of complex compounds in analytical chemistry.

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THIOUREA COMPLEXES OF LOW SOLUBILITY AND THEIR APPLICATION IN ANALYSIS

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Complex compounds with thiourea have attracted the attention of many investigators for a long time. After the first synthesis of thiourea complexes [1, 2, 3] which were of a rather haphazard nature, the classical investigations of Kurnakov [4,5] appeared. N. S. Kurnakov, who synthesized new complex compounds with thiourea, proved their structure and compared the thiourea complexes with other complex compounds and finally turned his attention to the fact that stable complexes are formed with metals which are precipitated in acid media by H_2S.

Thiourea complexes were further studied by Chugaev [7,8], Lebedinsky [9,10], Rosenheim and Meyer [6], Mahr and Ohle [11] and others. In the course of these investigations the order of the changes in stability of thiourea complexes was established [6] and a number of practically insoluble salts, consisting of complex cations and large anions were isolated [8,9,10,11].

Chugaev [7] was the first to use thiourea for analytical purposes (for isolating Os); further Mahr and Ohle [11] worked out a number of analytical methods based on the use of thiourea complexes.

Thiourea gives complex compounds with cations which possess a clearly defined tendency to form covalent bonds, and are characterized by large values of the difference between ionization potential and the heat of hydration [13]. Large complex cations of the type $[Me(CSN_2H_2)_n]^{z+}$ formed according to equation (1) should be precipitated by large anions [12,13] (e.g. tetrathiocyanodiamminochromite, tetranitrodiamminocobaltite, picrate, etc.).

$$Me^{z+} + \underline{n}CSN_2H_4 = [Me(CSN_2H_4)_n]^{z+} \qquad (1)$$

$$[Me(CSN_2H_4)_n]^{z+} + zX^- = [Me(CSN_2H_4)_n]X_z. \qquad (2)$$

In order to prove this, to 0.03 molar solutions containing the cations Ag^+, Tl^+, Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Bi^{3+}, Sb^{3+} [1], Fe^{3+}, Cr^{3+} and Al^{3+}, respectively was added a molar solution of thiourea, and afterwards to separate lots, saturated solutions of potassium picrate, ammonium tetrathiocyanodiamminochromite (Reinecke's salt) and ammonium tetranitrodiamminocobaltite (Erdman's salt) were added respectively. (The volume of solution taken amounted to approximately 0.3–0.4 ml). In the case of solutions of Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Sb^{3+}, Fe^{3+}, Cr^{3+}, and Al^{3+}, no precipitates were formed. While Ag^+, Tl^+, Cu^+, Hg^{2+}, Cd^{2+}, Pb^{2+}, and Bi^{3+}, which formed fairly stable complex cations with thiourea in solution, were precipitated by the large anions.

The crystal form of the precipitates was studied as well as the sensitivity of the reactions in drops of volume 0.003–0.004 ml. All the reactions were carried out in neutral or weakly acid solution, since precipitates of the sulfides of the respective metals are usually precipitated in alkaline media.

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[1] A solution of $SbCl_3$ in HCl was used.

The new compounds isolated were chemically analyzed and are described below.

1. COMPLEX BISMUTH SALTS

On addition of thiourea to a solution of bismuth nitrate, an intense yellow complex compound is formed. When a solution of Reinecke's salt is added to this crystals of characteristic form are precipitated (Fig. 1).[1)]

The salt corresponds to the formula $[Bi(CSN_2H_4)_6][Cr(NH_3)_2(CNS)_4]_3$. Concentration limit 1:18000; Limit of identification 0.17 µg.

Calculated (%)	Found (%)
Cr 9.63;	9.44; 9.50; 9.71.
CSN_2H_4 28.20;	28.27; 28.33; 28.42.

The action of Erdman's salt on the solution of the bismuth complex does not yield a precipitate. The picrate ion and Reinecke's salt both precipitate basic salts of Bi in the absence of thiourea (from concentrated solution).

2. COMPLEX MERCURY SALTS

From solutions of Hg salts Reinecke's salt separates intensely colored precipitates, which are practically insoluble in water and do not change appreciably on addition of thiourea. On addition of a solution of K picrate to a solution of $Hg(NO_3)_2$ and thiourea, characteristic crystals of the difficultly soluble salt of composition $[Hg(CSN_2H_4)_4](C_6H_2N_3O_7)_2$ (Fig. 2)[1)] separate out.

Concentration limit 1:35000; limit of identification 0.086 µg.

Calculated (%)	Found (%)
Hg 20.88;	20.86.
CSN_2H_4 31.64;	31.31.

3. COMPLEX CADMIUM SALTS

Solutions of Cd salts react with thiourea to form a fairly stable complex ion, which can be precipitated by picrate and Reinecke's salt. The addition of Erdman's salt to solutions of Cd not containing halides, does not lead to the formation of a precipitate.

The sensitivity of the reaction of formation of the tetrathiocarbammide-picrate is characterized as follows:

Concentration limit 1:91000; limit of identification 0.033 µg.

Calculated (%)	Found (%)
Cd 12.88;	12.79; 12.82.
CSN_2H_4 34.84;	34.83; 34.52; 34.55.

The composition corresponds to $[Cd(CSN_2H_4)_4](C_6H_2N_3O_7)_2$ (Fig. 3)[1)].

The formation reaction of the corresponding complex with Reinecke's salt is fairly sensitive. Concentration limit 1:135000; limit of identification 0.022 µg. The crystal form is depicted in Fig. 4.[1)]

The compound $[Cd(CSN_2H_4)_2]$ $[Cr(NH_3)_2(CNS)_4]_2$ was described by Mahr and Ohle [11]. On analysis we got different results, the composition being better represented by the formula $[Cd(CSN_2H_4)_4]$ $[Cr(NH_3)_2(CNS)_4]_2$, although in some preparations the content of the thiourea is lower. It is possible that in such a case a mixture of complexes is formed with different numbers of coordinated thiourea groups.

[1)] See Plate, page 79.

4. COMPLEX LEAD SALTS

Picrate precipitates a comparatively difficultly soluble salt of the composition $[Pb(CSN_2H_4)_4](C_6H_2N_3O_7)_2$ from solutions containing complex ions of Pb with thiourea. The pale yellow crystals formed have the form shown in Fig. 5.[1)]

Concentration limit 1:3200; limit of identification 1.43 µg. Analysis of the salt obtained gave the following results:

Calculated (%)	Found (%)
Pb 21.42;	21.03.
CSN_2H_4 31.43;	31.31.

Reinecke's salt precipitates Pb in the form of an amorphous precipitate which does not change significantly on the addition of thiourea. Addition of Erdman's salt to a solution of Pb and thiourea does not yield a precipitate.

5. COMPLEX THALLIUM SALTS

If thiourea and then picrate are added in that order to a solution containing Tl a crystalline precipitate is formed (Fig. 6).[1)]

The sensitivity of the reaction is given by the following result: Concentration limit 1:87000; limit of identification 0.035 µg.

The precipitate obtained was not analyzed.

Reinecke's salt precipitates an amorphous precipitate from solution of Tl; Erdman's salt does not form a precipitate with a solution of Tl salts or with the thiourea complex compound.

6. SILVER COMPLEX SALTS

Ag ions form very stable complex ions with thiourea of the composition $[Ag(CSN_2H_4)_2]^+$. On addition of picrate to a solution of an Ag salt containing excess thiourea, a characteristic crystalline precipitate is formed (Fig. 7).[1)]

This reaction is one of the most sensitive of known analytical reactions; in this case the concentration limit is 1:1500000 and the limit of identification 0.0027 µg. Halides do not interfere. The composition of the precipitate corresponds to the formula: $[Ag(CSN_2H_4)_2](C_6H_3N_3O_7)$ as the analytical results show.

Calculated (%)	Found (%)
Ag 22.10;	22.09; 21.98.
CSN_2H_4 31.14;	30.85.

The complex ions $[Ag(CSN_2H_4)_2]^+$ are precipitated also by Erdman's salt, forming characteristic crystals (Fig. 8).[1)]

The sensitivity of this reaction is considerably lower than the reaction with the picrate.

Concentration limit 1:9300; limit of identification 0.43 µg. The precipitate obtained dissolves in an excess of thiourea and behaves similarly to other thiorea complexes of Ag, e.g. $[Ag(CSN_2H_4)_2]Cl$. Apparently in such a case complex ions are formed in solution with a higher coordination number.

The reaction considered is specific for Ag, only Cu interferes. Result of the analysis was $[Ag(CSN_2H_4)_2][Co(NH_3)_2(NO_2)_4]$.

[1)] See Plate, page 79.

Calculated (%)	Found (%)
Ag 20.20;	19.86.
CSN_2H_4 28.47;	28.06.

Reinecke's salt precipitates an amorphous precipitate of $Ag[Cr(NH_3)_2(CNS)_4]$ which does not change appreciably on addition of thiourea.

7. COMPLEX COPPER SALTS

Salts of bivalent Cu are reduced by thiourea to thiourea complexes of univalent Cu. Picrates separate from solutions of these complexes, characteristic crystals (Fig. 9).[1)]

Concentration limit 1:43000; limit of identification 0.069 μg. The formula of this salt $[Cu(CSN_2H_4)_3](C_6H_2N_3O_7)$ was confirmed by analysis.

Calculated (%)	Found (%)
Cu 12.23;	12.12; 12.19; 12.23.
CSN_2H_4 43.88;	43.53; 43.79.

Erdman's salt does not precipitate thiourea complexes of Cu salts (I) but the Cu salts form an amorphous precipitate with Reinecke's salt.

A few results are compared in the following table.

Table

The precipitation of the thiourea complexes of metals by large anions

Thiourea complexes with ions	Limits of identification for anion action		
	picrate μg	tetrathiocyanoammino chromite, Reinecke's salt, in μg	tetranitrodiammino cobaltite, Erdman's salt, in μg
Bi^{3+}	not studied	0.17	no ppt.
Hg^{2+}	0.086	amorphous ppt.	"
Cd^{2+}	0.033	0.22	"
Pb^{2+}	1.43	amorphous ppt.	"
Zn^{2+}	no ppt.	"	"
Ag^{+}	0.0027	"	0.43
Tl^{+}	0.035	"	no ppt.
Cu^{+}	0.069	"	"

Consequently the formation of thiourea complex cations and their precipitation by large anions can be used for the detection of cations which have a tendency to form stable donor-acceptor bonds. Of the triple charge ions it is possible to detect only Bi^{3+} in this way; this is characterized by the largest value of the covalent characteristic (K = 290). Only complexes with covalent characteristics greater than 150 kcal are precipitated from solutions of double charged ions, containing excess thiourea, by large anions. The ion of Zn^{2+} with K = 136 kcal; although it forms complex compounds with thiourea in aqueous solution, these complexes are not precipitated by large anions, apparently as the result of a lack of stability in the complexes.

All unicharged ions having 18 or 18 + 2 electrons in the outer orbit have high values for the covalent characteristic and can be found in the form of thiourea complexes by means of large anions.

SUMMARY

1. New, practically insoluble complex compounds of thiourea with large anions in the outer spheres have been prepared: $[Bi(CSN_2H_4)_2][Cr(NH_3)_2(CNS)_4]_3$; $[Hg(CSN_2H_4)_4](C_6H_2N_3O_7)_2$; $[Cd(CSN_2H_4)_2](C_6H_2N_3O_7)_2$; $[Pb(CSN_2H_4)_4](C_6H_2N_3O_7)_2$; $[Ag(CSN_2H_4)_4](C_6H_2N_3O_7)$; $[Ag(CSN_2H_4)_2][Co(NH_3)_2(NO_2)_4]$; $[Cu(CSN_2H_4)_3](C_6H_2N_3O_7)$.

2. The compounds prepared have characteristic crystalline forms. The formation of such compounds can be used for the detection of Bi^{3+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+}, Tl^{+} microcrystalloscopically. The sensitivity of these reactions was determined.

3. The formation of thiourea complexes in solution and their precipitation by large anions is a reaction typical for cations with a large covalency characteristic [13].

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THE APPLICATION OF MATHEMATICAL METHODS FOR EVALUATING THE RESULTS OF CHEMICAL ANALYSIS[1)]

E. G. Gracheva

The increased demands of our country's industry for high grade analyses compells us to reexamine the mathematical methods used by analysts for evaluating the errors of their results. In a number of cases, e.g. in the calculation of the magnitude of the permissible variation between the results of parallel batches in standard analysis, the approximate evaluation of the errors should be replaced by exact calculations. In order to achieve this it is recommended that the methods of contemporary mathematical statistics be used.

The proposed methods of mathematical treatment can be applied only to errors which are of a random character, i.e. the errors are distributed along a Gaussian curve. The methods are based on the application of new methods from the theory of errors developed by Romanovsky [1]. The advantage of this method as compared with older methods is that it gives more accurate results in the evaluaton of a small number of observations. These methods enable systematic errors (the absence of which ensures the "correctness" of the analytical method employed) to be exposed, by establishing the reality of the deviations between results obtained by different analytical methods, and by discarding results which are distorted by coarse errors.

Since we have not decided on the final choice of terms which reflect the effect of different kinds of errors in results obtained by any method, in any subsequent use of the term "precision"[2)] for the characterization of the method or result, we have in view only errors (mistakes) of a random nature.

I. THE QUANTITATIVE EVALUATION OF THE PRECISION OF A METHOD

The precision of a method is established from n replicate analyses of one and the same material and is characterized by the root mean square value of the error of one single determination, calculated according to the following formula:

$$S = \pm \sqrt{\frac{(a-x_1)^2 + (a-x_2)^2 + \cdots + (a-x_n)^2}{n-1}} \qquad (1)$$

where a is the arithmetic mean, x_1, $x_2 \ldots$, x_n – the analytical results, n is the number of analyses.

For characterization of the precision of a method it is more convenient to express the root mean square value as a percentage, i.e. in the form

$$\frac{S}{a} 100\%. \qquad (1a)$$

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1) A report read at the Conference on Classical Methods of Chemical Analyses held in Moscow, November 14-17, 1951.

2) The choice of this term instead of the more often used "reproducibility" is based on the fact that in metrology and the mathematical theory of errors it is applied to the same category of errors, i.e. to random errors.

In many cases it is necessary to indicate the limits for a change in the magnitude of the error of a single observation, e.g. for evaluation of the permissible variation between results obtained by one method. In such a case the width of the limits will be connected with the probability of finding errors within these limits. (This probability is often called the "confidence" and is designated by α). Thus from the classical theory of probability, it is known that the random error of a single measurement can be greater than the root mean square value S in 32% of all cases (which corresponds to a confidence $\alpha = 0.68$%), greater than 2S in 5% of all cases ($\alpha = 0.95$) and greater than 3S in only 0.3% ($\alpha = 0.99$).

The possibility of applying the classical methods of calculating errors is excluded for a small number of errors. The methods of contemporary methematical statistics specially developed for a small number of observations must be used instead.

The value of the smallest error of a single observation in this case is expressed in the form $t_\alpha S$, where the factor t_α depends not only on the confidence α but also on the number of experiments (n).

Tables are available [1,2,3] in which the numerical values of t_α for different α from 0.1 to 0.999 and $k = n - 1$ from 1 to infinity are given.

For the same value of α, the magnitude of t_α decreases with increase in k, e.g.

at $\alpha = 0.95$ for	$n = 3$	$t_\alpha = 4.3$	at $\alpha = 0.99$ for	$n = 3$	$t_\alpha = 9.9$
	$n = 5$	$t_\alpha = 2.8$		$n = 10$	$t_\alpha = 3.2$
	$n = 10$	$t_\alpha = 2.3$		$n = 20$	$t_\alpha = 2.9$
	$n = 20$	$t_\alpha = 2.1$			

From this it follows that the width of the interval for all possible values of the error of a single observation (for a definite confidence) can be evaluated more accurately, the greater the number of results used for calculating the root mean square error. This also holds for the accuracy of the determination of S itself, and should be borne in mind in selecting the number of results for characterization of the precision of a method. The table of values for the relative errors (q) for the root mean square error (S) given by Romanovsky [1], shows that for

$\alpha = 0.95$ for	$n = 3$	$q = 340$%	at $\alpha = 0.99$ for	$n = 3$	$q = 998$%
	$n = 6$	$q = 109$%		$n = 6$	$q = 200$%
	$n = 21$	$q = 36$%		$n = 21$	$q = 56$%

Thus the accuracy of S itself obtained from 6 parallel results amounts to only ca. 100% for a confidence of 0.95.

II. EVALUATION OF ANALYTICAL RESULTS AND CALCULATION OF THE RESULTS WHEN GREAT PRECISION IS REQUIRED.

a) The arithmetic mean $\underline{a}$ obtained from the results $x_1, x_2, \ldots, x_n$ of all the analyses carried out can serve as a result, with an indication of the value of the error calculated for a definite confidence - α. It is necessary to indicate the number of analyses n and the value of the confidence used in order to evaluate the error. (Elimination of results which are obviously spurious from a series of observations can only be carried out by the method given below.)

The answer is given in the following form:

$$A = a \pm t_\alpha \frac{S}{\sqrt{n}} \qquad \text{or} \qquad A = a \pm t_\alpha \frac{S}{a\sqrt{n}}\ 100\% \qquad (2)$$

where S is the root mean square error

t_α is the factor depending on the number of analyses n and the confidence $\alpha = 0.95 - 0.99$ found from tables.

b) If for the analyses a method is employed the precision of which has been determined beforehand, i.e. the value of S is known, then it is possible to indicate in advance what number of parallel determinations it is necessary to carry out in order to get a result with a permissible error. Let the precision of any method be expressed in percentages by the quantity $\frac{l}{a} = \frac{S}{a}\ 100\%$.

If e.g. it is required to determine the content of any element in a test with an error not greater than p%, then from the formula given above it follows that

$$p = \frac{t_\alpha S}{a\sqrt{n}}\ 100\% \qquad \text{whence} \qquad n = t_\alpha^2 \left(\frac{l}{p}\right)^2 \qquad (3)$$

Taking the value t_α from the tables [1], we find:

1) $\alpha = 0.95$ for $\frac{p}{l} = 1$ $n = 7$ 2) $\alpha = 0.99$ for $\frac{p}{l} = 1$ $n = 11$

$\frac{p}{l} = 0.5$ $n = 18$ $\frac{p}{l} = 0.5$ $n = 31$

$\frac{p}{l} = 0.1$ $n = 387$ — $\frac{p}{l} = 0.1$ $n = 668$

It follows that it is very difficult in practice to get an error with sufficient confidence, which exceeds the precision of the method employed.

III. COMPARISON OF TWO RESULTS AND THE ELIMINATION OF RESULTS WHICH ARE OBVIOUSLY SPURIOUS FROM A SET OF OBSERVATIONS.

a) Comparison of two results a_1 and a_2, obtained, e.g. for one and the same test by different analysts in different laboratories or by different methods. We assume that in one series n_1 analyses were carried out and the average value obtained is a_1. In another series n_2 analyses were performed and the mean obtained a_2.

It is required to explain whether the deviation between the means of the 2 series is the consequence of random errors which are related to the accuracy of the methods, or the results of the two series are essentially different, i.e. in one of the methods at least the error is systematic.

The answer can be obtained from the following formulas.

$$t = \frac{a_1 - a_2}{S_0\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \qquad (4)$$

where

$$S_0 = \sqrt{\frac{(n_1-1)S_1^2 + (n_2-1)S_2^2}{n_1 + n_2 - 2}}$$

S_1 and S_2 are the root mean square errors from the two sets. The numerical value of $\underline{t}$ for a chosen confidence α is found from the tables for $\underline{t}$ [1] in this case $k = n_1 + n_2 - 2$.

If after substitution in formula (4) of the values $\underline{a}_1$, $\underline{a}_2$, $\underline{S}_0$ it appears that the value of t_α is greater than or equal to the tabular value of t_α for given values of α and $\underline{k} = n_1 + n_2 - 2$ it follows that the deviation between comparable values is not random and they must be considered as essentially different.

b) Elimination of results which are obviously spurious can be carried out by the formula given above (4).

Let there be $\underline{n} + 1$ results:

$$x_1, x_2 \ldots . x_n, x_{n+1}.$$

The question posed is whether x_{n+1} is a true result or not, and whether it can be eliminated. The following method is employed. For a series of $\underline{n}$ results which does not include the doubtful result x_{n+1}, the arithmetic mean $\overline{x}_n$ and the root mean square S are calculated for the $\underline{n}$ results.

The values found are substituted in formula (4) in which $\underline{a}_1 = x_{n+1}$ and $\underline{n}_1 = 1$.

From which it follows that it is difficult in practice to get an error exceeding the precision of the method employed. The same procedure as above is adopted with the result obtained after substitution in the formula. If the deviation between $\overline{x}_n$ and x_{n+1} is not random, then the result x_{n+1} can be eliminated from the series of observations since it is spurious.

We intend to include examples of the application of the methods given above for the evaluation of numerical data obtained by chemical analysts in a future article.

In the literature cited above numerous examples are given, chiefly from technical subjects.

SUMMARY

1. In evaluating the results of a small number of analyses it is necessary to use the new mathematical statistics.

2. The quantitative evaluation of the precision of an analytical method is accomplished by means of the root mean square error, expressed in %, with an indication of the number of analyses from which this value was calculated.

3. The precision of a result (arithmetic mean) obtained by analysis is evaluated for a confidence $\alpha \geqslant 0.95$ according to the root mean square with an indication of the number of replicate experiments.

4. For a small number of results the error calculated by the new statistics is always greater than that calculated from the classical methods.

5. Systematic errors can be detected only by comparison of results obtained by different analytical methods, for conditions where the errors of comparable results or the precision of the methods used are known.

6. A criterion is given for elimination of obviously spurious results.

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MICROCRYSTALLOSCOPIC REACTIONS FOR NITRATES AND NITRITES

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A few microcrystalloscopic reactions for nitrates and nitrites are described in the literature. Solutions of nitron and of berberine sulfate in acetic acid form crystalline precipitates with solutions of nitrates and nitrites. These reactions are sensitive (limits of identification from 0.005 to 0.4 μg NO^-_3 NO^-_2) but not specific. In order to increase the specificity of the reaction for nitrite it is carried out in a gas cell. The formation of a crystalline precipitate $K_2PbCu(NO^-_2)_6$ when solutions of nitrites are mixed with acetic acid solutions of the acetates of K, Pb and Cu is also used, but the reaction though specific is of low sensitivity [1].

During the study of the analytical properties of certain mercuri-ammino compounds of the aromatic and heterocyclic series, we worked out several microcrystalloscopic reactions for nitrates and nitrites.

There is no information in the literature on the microcrystalloscopic reactions with mercury organic compounds. We found only a reference to the composition of some crystalline precipitates which are formed during the reaction of metallo-organic compounds with nitrates and nitrites [2]. This enabled us to apply some mercury organic compounds for the microcrystalloscopic reactions for anions.

REACTIONS FOR NITRATES

The reagent which we used was a saturated aqueous solution of 1,4-aminophenylmercuriacetate, which we synthesized according to a method described in the literature [3]; with aqueous nitrate solutions it forms characteristic crystalline precipitates of the composition $H_2NC_6H_4HgNO_3$ in the form of colorless, sharply profiled rosettes of X-shaped crystals, the prisms had sizes up to 170μ. The precipitate settles out from dilute solution on rubbing with a glass rod (Fig. 1). [1])

Limit of identification 0.3 μg NO^-_3.
Concentration limit 1:7000.

The pleocroism of crystals of 1,4-aminophenylmercuriacetate is intense (yellow, red); the extinction angle of the prisms is 7-8°. Ions of Cl^-, Br^-, I^-, CN^-, CNS^-, NO_2^-, S^{2-}, SO_3^{2-}, SO_4^{2-} and some other ions interfere with the reaction. Cl' and SO_4^{2-} also form characteristic crystalline precipitates; Cl' fine transparent rosettes, SO_4^{2-} large rosettes of serrated laminas.

In the presence of nitrites the reaction was performed as follows: to 1-2 drops of the test solution is added a drop of a saturated solution of meta, or better ortho, nitraniline, and the mixture acidified with a drop of 10% acetic acid. On addition of a drop of the solution thus prepared to a drop of the reagent, it is possible to observe the formation of crystals of 1,4-aminophenylmercurinitrate after 5-7 minutes. An amount of NO_2^- equivalent to 20 times that of NO_3 ions (for 0.8 μg NO_3^-) does not interfere.

[1]) See Plate, page 79.

Nitrates can be detected in solutions containing other ions after these ions have been removed. To 1-2 drops of the test solution a drop of an aqueous solution of Ag acetate (for separation of Cl^-, Br^-, I^-, CN^-, CNS^-) or a drop of a 10% solution of lead acetate (for removal of S^{2-}, SO_3^{2-}, SO_4^{2-}), respectively are added. The solution is then centrifuged and a drop of reagent added to a drop of the transparent centrifugate. The formation of crystals of 1,4-aminophenylmercurinitrate is studied microscopically. It is possible to detect NO_3^- ions (2-3 μg) in the presence of a tenfold excess of interfering ions after their removal by the method just described. Crystals of the reagent and of 1,4-aminophenylmercurinitrate differ appreciably from each other. The crystals of reagent which settle out when a drop dries out consist of colorless parallellograms and rhombic prisms (Fig. 2).[1] The pleochroism of reagent crystals is intense (yellow, red, green); the extinction angle for the crystals is 40°.

Reactions for Nitrites

Eight of the mercury organic compounds which we examined form crystalline precipitates with nitrites viz: 1,4-aminophenylmercuriacetate $H_2N \cdot C_6H_4HgAc$; 1,4-methylaminophenylmercuriacetate $(CH_3)NH \cdot C_6H_4HgAc$; 1,4-ethylaminophenylmercuriacetate $(C_2H_5)NH \cdot C_6H_4HgAc$; 1,4-dimethylaminophenylmercuriacetate $(CH_3)_2N \cdot C_6H_4HgAc$; 1,4-diethylaminophenylmercuriacetate $(C_2H_5)_2N \cdot C_6H_4HgAc$; 2-chloro-1,4-aminophenylmercuriacetate $Cl(NH_2)C_6H_3HgAc$; 2-aminopyridine-5-mercuriacetate $C_5H_3N \cdot (NH_2) \cdot HgAc$; and quinolinemercuriacetate $C_9H_6N \cdot HgAc$.

Some of these compounds either did not form crystalline compounds with solutions of nitrites when a gas cell was used or gave insensitive reactions that makes their application as reagents for nitrites difficult. Detection of nitrites can be carried out in a gas cell with 1,4-aminophenylmercuriacetate; 1,4-methylamino-and 1,4-ethylaminophenylmercuriacetates, and quinolinemercuriacetate. Acetic acid solutions of 1,4-methylamino-and 1,4-ethylaminophenylmercuriacetate form crystalline precipitates of nitrosamines with nitrites [2], aqueous and acetic acid solutions of quinolinemercuriacetate form a precipitate of the corresponding nitrite. 1,4-Aminophenylmercuriacetate does not give a crystalline precipitate with solutions of nitrites when the reaction is carried out in a gas cell, but if the NO_2^- separated out from its acid solution is oxidized to NO_3^- then the presence of NO_2^- can be established by the reaction for nitrates.

In Table 1 results are given which characterize the crystalline precipitates which are formed when these reagents react with nitrite solutions (in a gas cell).

These reactions were carried out as follows; a drop of the test solution was placed at the bottom of the gas cell and acidified with a drop of 10% acetic acid. The cell was covered with a glass plate on the lower surface of which a drop of a mixture of 1,4-aminophenylmercuriacetate and H_2O_2 had been placed (4 vols. of a saturated aqueous solution of 1,4-aminophenylmercuriacetate and 1 vol. H_2O_2). The NO_2 liberated from the drop was oxidized by the H_2O_2 to NO_3^-. After 2-3 minutes the drop on the upper glass of the cell was combined with a drop of the reagent (without H_2O_2) and 1,4-aminophenylmercurinitrate was formed, predominantly in the form of prisms, and rods up to 50 μ in size. I^-, CN^-, CNS^- interfere, therefore, they must be removed beforehand as described above. I^- interferes because of the formation of free I_2 according to the reaction:

$$2NO_2^- + 2I^- + 4H^+ = I_2 + 2NO + 2H_2O.$$

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1) See Plate, page 79.

Table 1

Characteristics of Crystalline Precipitates

	Reagent		
	1,4-methylamino-phenylmercuri-acetate	1,4-ethylaminophenyl-mercuriacetate	Quinolinemercuri-acetate
Solvent	8% acetic acid	6% acetic acid	Water
Color, form of crystalline ppt.	Colorless, pale yellow plates, rosettes, needles	Pale yellow plates and rosettes	Colorless six-sided rods, rosettes
Composition of ppt.	$CH_3(NO)N \cdot C_6H_4HgAc$	$C_2H_5(NO)N \cdot C_6H_4HgAc$	$C_9H_8N \cdot HgNO_2$
Limit of identification in μg	0.6	1.6	0.6
Max. crystal size in μ	250	200	300
Pleocroism of ppt. crystals	Weak (yellow)	Weak (yellow)	Intense (yellow, red, green)
Extinction angle	15-17°	90°	40°

Limiting ratios when reaction occurs in gas cell

NO_2^-: Cl^- (or Br^-, NO_3^-, SO_4^{2-}) = 1:100 for 1μg NO_2^-
NO_2^-: I^- (or CN^-, CNS^-, SO_3^{2-}) = 1:50 for 1μg NO_2^-
NO_2^- : S^{2-} = 1:25 for 1.5 μg NO_2^-.

Saturated solutions of 1,4-methylamino- or 1,4-ethylaminophenylmercuriacetate (obtained according to [2]) in 6-8% acetic acid, form crystalline precipitates of the respective nitrosamines with nitrites in acetic acid solutions. It is possible to observe the appearance of crystals of the nitrosamines in a drop of the reagent placed on the lower side of the cover slide of the gas cell, 5-12 minutes after the acidification of the test solution. The crystals appear faster, the smaller the drop of reagent (Fig. 3[1] for the reaction product with 1,4-methylaminophenylmercuriacetate, Fig. 4[1]) with 1,4-ethylaminophenylmercuriacetate). When 1,4-ethylaminophenylmercuriacetate is used, particularly in dilute solutions of nitrites, the reaction proceeds better, if 3-4 minutes after acidification of the drop of test solution, the cover glass of the gas cell is removed. The formation of crystals can then be observed 3-4 minutes after removal of the glass. A saturated aqueous solution of 1,4-ethylaminophenylmercuriacetate also forms crystalline precipitates with nitrite solutions, in the form of colorless prisms up to 60 μ. This reaction is very slow when a gas cell is used. Interfering ions (Cl^-, Br^-, I^-, CN^-, CNS^-, S^{2-}, SO_3^{2-}, SO_4^{2-}), must be removed beforehand by the method described above.

The limiting ratios for the reactions with 1,4-methylaminophenylmercuriacetate in a gas cell are as follows:

NO_2^-: Cl^- (or Br^-, CNS^-, NO_3^-, SO_4^{2-}) = 1:100 for 1.6 μg NO_2^-
NO_2^-: I^- (or CN^-, SO_3^{2-}) = 1:50 for 1.6 μg NO_2^-
NO_2^- : S^{2-} = 1:50 for 3.2 μg NO_2^-

The limiting ratios for reactions with 1,4-ethylaminophenylmercuriacetate are half as much.

[1]) See Plate, page 79.

A saturated aqueous solution of quinolinemercuriacetate (m.p. 155°) rapidly forms a crystalline precipitate of quinolinemercurinitrite (Fig.5)[1] with nitrites (in a gas cell). Under the same conditions but with an acetic acid solution of the reagent, the formation of a crystalline precipitate is considerably slower. In aqueous solution, without a gas cell the sensitivity of the reaction is higher; limit of identification 0.2 μg NO_2^- (in a gas cell it is 0.6 μg). The limiting ratios for reactions in a gas cell are the same as for the reactions with 1,4-ethylaminophenylmercuriacetate.

The crystals of reagents which settle out on the drying of a drop differ appreciably from the crystals of the reaction products of mercury organic compounds with nitrites. Results are given in Table 2 which characterize the crystals of 1,4-methylamino- and 1,4-ethylaminophenylmercuriacetate, and quinolinemercuriacetate which form on the drying out of drops containing them.

It should be noted that drops of the reagent solution dry out slowly in a gas cell and separation of crystals can be observed only after an interval of 10-12 hours.

Table 2

Characteristics of Reagent Crystals

	Reagent		
	1,4-methylamino-phenylmercuri-acetate	1,4-ethylaminophenyl-mercuriacetate	Quinolinemercuri-acetate
Color, form of reagent crystals	Colorless clusters of fine needles and small plates	Colorless clusters of plates	Colorless clusters of rods and plates
Pleochroism of the reagent crystals	Weak (yellow)	Weak (yellow)	Weak (yellow, red, green).
Extinction angle of crystals	90°	15-17°	90°

SUMMARY

1. A microcrystalloscopic reaction for nitrates with 1,4-aminophenylmercuriacetate is proposed. Some crystallo-optic constants of crystals of 1,4-aminophenylmercurinitrate are adduced. The limit of identification is 0.3 μg NO_3. This reagent can also be used for detecting nitrites by means of a gas cell, after oxidation of the NO_2 separating out of an acid solution to NO_3^-.

2. Three reagents are proposed for the microcrystalloscopic identification of nitrites, namely, 1,4-methylamino- and 1,4-ethylaminophenylmercuriacetates and quinolinemercuriacetate. Some crystallo-optic constants are given for the respective nitrosamines and for quinoline mercurinitrite. The limits of identification when the reactions are carried out in a gas cell are 0.6-1.6 μg NO_2^-.

3. Ions which interfere with the reactions for the nitrates and nitrites (Cl^-, Br^-, I^-, CN^-, CNS^-, S^{2-}, SO_3^{2-}, SO_4^{2-}), are removed by means of Ag and Pb acetates, and the NO_2^- ions are masked by addition of ortho or metanitraniline, whereby the effect of excess interfering ions can be reduced.

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[1]) See Plate, page 79.

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NEW AZO-INDICATORS OF THE METHYL ORANGE SERIES, AND THE RELATION BETWEEN THE STRUCTURE AND pH CHANGES OF AZO-INDICATORS [1)]

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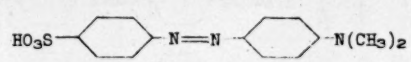
At a time when intensive search is being carried out for new organic reagents for the detection of different metallic ions and new methods for developing such researches are being worked out, due attention is still not given to research for indicators for H^+ ions, i.e. pH-indicators. Meanwhile the demand for new pH-indicators, particularly for strong acid solutions is becoming urgent.

pH-Indicators of different structures possess unequal value in practice. Recently attention was given to one factor, to which little significance has been attached hitherto, namely, if the molecule of a pH-indicator contains even only two salt or complex forming groups, and these are disposed in such a manner that they can form cyclic salts with metal ions, then such a pH-indicator can under suitable conditions give color reactions with metals, which are quite appreciable even in very dilute solutions. The colors that develop in such a case distort the color of the pH-indicator and lead to a very substantial " salt effect of a special kind" [1]. Some pH-indicators tend in addition to give colored "solid phase" reactions [2], which also makes the indicators unsuitable in the presence of a number of elements.

These errors are not characteristic of azo-indicators which contain amino or hydroxy groups in the para position with respect to the azo-group, e.g. the substituted p-dimethylaminoazobenzene-p'-sulfonic acid (methyl orange).



The present investigation is devoted to a search for new pH-indicators among the substituted p-dimethylaminoazobenzene-p'-sulfonic acids.

There are some references to the study of the relation between structure and pH change for azo-indicators in the literature, e.g. Thiel [6], Blumberger [7] and Glockner [8].

In these investigations the values of the pH are compared with the structure and values of the pH given for which the indicators are in the semi-acid form (pK). Unfortunately the conclusions from these investigations do not give a sufficiently clear picture to serve as a basis for a search for new pH-indicators with the given pH value changes.

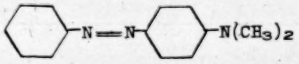
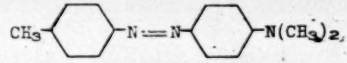
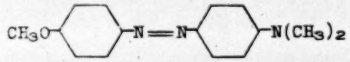
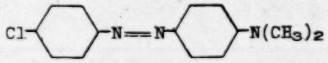
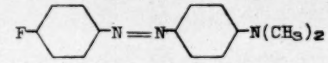
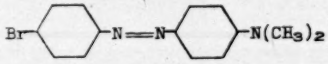
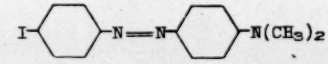
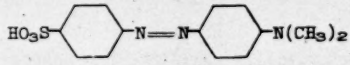
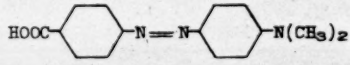
The overall picture is as follows. The introduction of positive substituents ($-NH_2$, $-OCH_3$, $-OH$) increases the pK value somewhat, while the introduction of negative substituents ($-NO_2$, $-SO_3H$, $-COOH$) decreases the pK. But the extent of the shift is small, the interval between extreme pH values is only 0.5 pH units.

[1)] Extract from a dissertation by G.N.Kosheleva.

Our research on a series of substituted p-dimethylaminoazobenzenes showed that in this case the effects of positive and negative substituents, in general are similar and rather small in their absolute values (Table 1). Nevertheless we observed that strongly acid salt forming groups ($-SO_3H$, $-COOH$) do not decrease but actually increase pH.

Table 1

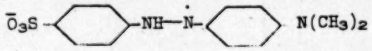
The Effect of Substituents on pK for Azo-indicators of the p-Dimethylaminoazobenzene Series

No.	Formula	pK in 50% alcohol	Magnitude of pK displacement in pH units as compared with No.1.
1		1.98	-
2		2.06	+0.08
3		2.15	+0.17
4		1.70	−0.28
5		1.68	−0.30
6		1.70	−0.28
7		1.72	−0.26
8		2.16	+0.18
9		2.10	+0.18

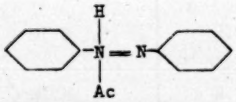
Thus for this particular series of pH-indicators the displacement of pK arising from the effect of positive and negative substituents in the para position to the azo group is small.

Greater displacements of pK can be achieved when other factors are considered.

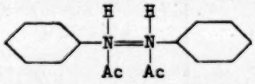
The change in color of aminoazo compounds in going from alkaline to acid media is connected with salt forming azo groups (formation of "azo salts"). Several methods of representing the azo-salts formed in acid solutions have been proposed and many hypotheses exist regarding their structure, e.g. V. Diltei and R. Vitsinger consider azo-salts to be compounds containing a coordinatively unsaturated nitrogen, and represent their structure as follows [3]:



F. Kerman proposes the following structures [4]:



or



(Ac = acid radical)

Whichever method may be used for depicting the structure of azosalts, it is clear that in order to facilitate the formation of azo-salt, the azo-group must be opened up, while none of the substituents which are spatially near to the azo-group should impede the approach of the proton to the nitrogen of the azo-group.

From this point of view, the presence of substituents near the azo-group should impede salt formation and therefore lead to a decrease in the value of pK.

Experiment showed that this actually occurs. By the introduction of groups which sterically hinder salt formation of the azo-group the pK value is decreased. The absolute value of the decrease in pK in this case is considerably greater than that which results from the introduction of the negative substituents mentioned above in other positions in the molecule of the azo-compound. Steric hindrance as a result of substituents is most clearly manifested for the case of indifferent substituents, since the influence of other factors is not superimposed on their action. But substituents in the ortho position to the azo-group exert a definite effect on pK whatever the nature of the substituent.

The relation mentioned above is shown very clearly here. Salt-forming substituents in the ortho position to the azo-group, do not decrease pK, in contrast to non-salt-forming substituents, but on the other hand increase it. It is possible that salt-forming substituents facilitate proton donation to the azo-group and therefore azo-salts are formed in less acid solutions.

This method of lowering pK by a considerable amount enables a series of new pH-indicators to be synthesized for low pH values.

In the present article we shall describe new pH-indicators of the methylorange series. New indicators of the tropeoline OO series (diphenylamine substituted-<4-azo-1>-benzene-4-sulfonic acids) described by G.N. Kosheleva in her dissertation are also very interesting.

TABLE 2

Effect of Substituents in the Ortho Position to the Azo Group on pK

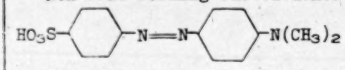
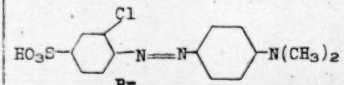
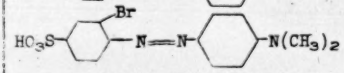
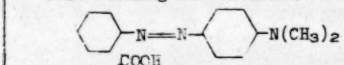
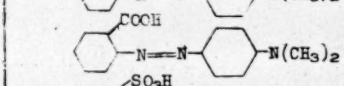
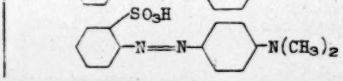
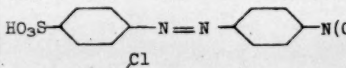
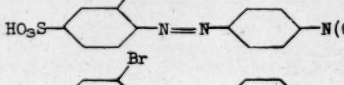
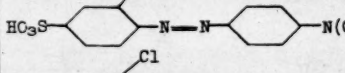
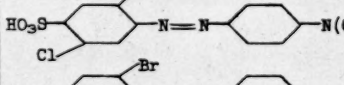
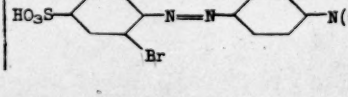
No.	Formula	pK	Magnitude of pK shift as compared with No. 1– in pH units
	Non salt-forming substituents		
1		3.37	–
2		2.70	–0.67
3		2.73	–0.64
	Salt Forming Substituents		As compared with No. 4
4		3.28	—
5		5.40	+3.12
6		3.85	+0.57

TABLE 3

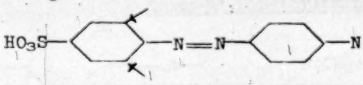
New Indicators of the Methylorange series; Acid solutions - rose, neutral and alkaline - yellow

No.	Formula	pK	Range of pH change in pH units	Range of pH change in N HCl
1		3.37	3.1-4.5	0.00005-0.001
2		2.70	1.6-3.7	0.025-0.00020
3		2.73	1.6-3.6	0.025-0.00025
4		2.3	1.4-3.2	0.04-0.001
5		-	-0.5	-0.4

The deliberate use of steric hindrance can serve as a guide for improving the selective action of analytical reagents. We shall discuss these ideas in a special article.

New pH-Indicators of the Methylorange Series

The new indicators of this series which are described differ from methyl orange.



in that they have halogen atoms in the positions indicated by the arrows.

These indicators closely resemble methylorange externally. They are soluble in water and form colors which are similar to that of methylorange, yellow in neutral and alkaline media and rose in acid.

Different stable imitative colors, e.g. colors of solutions of iron and cobalt salts, proposed by Kolthoff or Taube [5], which are used for comparison with methylorange can therefore be used for the new indicators. The pH values of course are different.

These indicators also resemble methylorange in that they are free from some salt errors which arise from the presence of traces of multivalent elements [1], and also like methylorange they do not easily tend to give colored solid phase reactions [2] and therefore are suitable for all kinds of inorganic analysis.

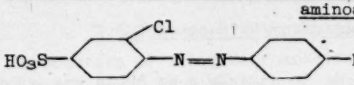
The colors formed by the new indicators are completely stable both in alkaline and in acid solution and in this connection possess a definite advantage over some other indicators used for low pH values such as methylviolet and malachite green, the colors of which in acid solution are quickly decolorized and tend to give colored solid phase reactions with heavy anions, so they are unsuitable in many cases.

In addition, the colors of the new indicators, like that of methylorange, can if necessary be easily destroyed by strong reducing and oxidizing agents (elemental Br, Cl, $KMnO_4$). H_2O_2 has no effect on the indicators.

The pK values and the range of pH changes for these indicators are given in Table 3.

The new indicators cannot be prepared by direct bromination or chlorination of methylorange, but are easily synthesized by the methods described below.

Synthesis of New pH-Indicators of the Methylorange Series 2-Chloro-4'-Dimethylaminoazobenzenesulfonic Acid-4



$C_{14}H_{14}O_3N_3ClS$ (M = 339.8)

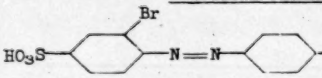
A solution of 4.5 g of o-chloroaniline-p-sulfonic acid in the form of its Na salt and 1.6 g $NaNO_2$ in 5 ml H_2O are poured into a mixture of 10 ml conc.HCl and 15 g ice. 2.6 g dimethylaniline in 10 ml dil. HCl (1:2) is added to the suspension of diazonium salt obtained and to the final mixture a conc.solution of Na-acetate is added dropwise with stirring, till there is no further acid reaction to Congo paper.

The 2-chloro-4'-dimethylaminoazobenzenesulfonic acid-4 which separates out

is filtered off and is twice recrystallized from alcohol. The crystals are orange.

5.310 mg substance: 0.499 ml N_2 (753 mm, 21°)
4.300 mg substance: 0.417 ml N_2 (753 mm, 21°)
Found % N: 10.81, 11.07
$C_{14}H_{13}O_3N_3ClSNa$. Calculated % N: 11.01

2-Bromo-4'-Dimethylaminoazobenzenesulfonic Acid-4



HO_3S—(Br)—N=N—$N(CH_3)_2$; $C_{14}H_{14}O_3N_3BrS$. (M = 284.3)

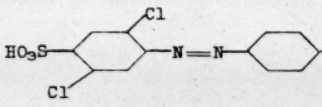
A solution of 4.1 g o-bromosulfonic acid as its Na salt and 1 g of $NaNO_2$ in 30 ml H_2O are poured into a mixture of 5 ml conc. HCl and 20 g of melting ice. The diazonium suspension formed is poured into a solution of 1.8 dimethylaniline in 10 ml alcohol. After 1 hour standing the product which separates out is filtered and recrystallized first from H_2O and then from alcohol. The crystals are yellow-orange in color.

4.745 mg substance: 0.446 ml N_2 (756 mm, 22°)
4.670 mg substance: 0.436 ml N_2 (757 mm, 22°)
Found % N: 10.83, 10.73
$C_{14}H_{13}O_3N_3BrSNa$. Calculated % N: 10.93

2,5-Dichloro-4'-Dimethylaminoazobenzenesulfonic Acid-4

A solution of 1.1 g of dichlorosulfanilic acid as the Na salt in 10 ml H_2O and 0.3 g of $NaNO_2$ are poured into a mixture of 10 ml conc. HCl and 10 g melting ice. The suspension of diazonium salt thus obtained is gradually added with stirring to 0.51 g of dimethylaniline dissolved in 5 ml alcohol and mixed for 1 hour. The 2,5-dichloro-4'-dimethylaminoazobenzenesulfonic acid-4 which separates out is filtered and dried. The yield was 2 g and it was recrystallized from H_2O and alcohol. The crystals were of an orange-yellow color.

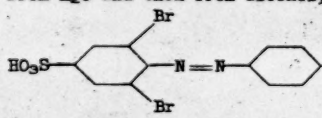
0.2034 g substance: 16.34 ml 0.1 N HCl
0.1536 g substance: 12.26 ml 0.1 N HCl
Found % N: 11.24; 11.17
$C_{14}H_{12}O_3N_3Cl_2SNa$. Calculated % N: 11.19



HO_3S—(Cl)—N=N—$N(CH_3)_2$; $C_{14}H_{13}O_3N_3Cl_2S$; (M = 375.2)

2,6-Dibromo-4'-Dimethylaminoazobenzenesulfonic Acid-4

A solution of 1.5 g dibromosulfanilic acid as its Na salt in 10 ml H_2O and 0.3 g $NaNO_2$ are added to a mixture of 10 ml conc. HCl and 10 g melting ice. The suspension of diazonium salt thus obtained is added gradually with stirring to a solution of 0.51 g dimethylaniline in 15 ml alcohol. After 1 hour's mixing the 2,6-dibromo-4'-dimethylaminoazobenzenesulfonic acid-4 which separates out is filtered off. The weight of product obtained was 1.9 g. After recrystallization from H_2O and then from alcohol, the crystals obtained were orange-yellow in color.



HO_3S—(Br)(Br)—N=N—$N(CH_3)_2$; $C_{14}H_{13}O_3N_3Br_2S$; (M = 464.2)

4.830 mg substance: 0.404 ml N_2 (730 mm, 22°)
5.250 mg substance: 0.442 ml N_2 (754 mm, 23°)
Found % N: 9.11, 9.35
$C_{14}H_{12}O_3N_3Br_2SNa$. Calculated % N: 9.10

SUMMARY

1. The introduction of positive ($-NH_2$, $-OCH_3$) or negative ($-NO_2$, $-COOH$, $-SO_3H$) substituents in the meta or para position to the azo group in the molecule of p-dimethylaminoazobenzene-p-sulfonic acid (methylorange) gives rise to only a relatively insignificant displacement of pK.

2. A considerably greater shift is observed in pH when indifferent substituents (-Cl, -Br), giving rise to steric hindrance are introduced into the ortho position relative to the azo-group.

3. The new indicators described are chloro- or bromo-substituted methylorange; they are similar to methylorange in color, but are suitable for more acid solutions, pH 1.6 to 3.7.

4. The syntheses of some new pH-indicators are described.

Received July 31, 1951

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[3] R.Vitsinger, Organic Dyes. Introduction to the chemistry of dyes on the basis of the coordination theory. Leningrad, 1936, p. 46.

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Obituary

MIKHAIL MAKSIMOVICH FAINBERG

Mikhail Maksimovich Fainberg, a member of the Commission on Analytical Chemistry in the USSR Academy of Sciences, died on the 14th of October 1951. His was an untimely death.

Since he was one of the foremost specialists in the field of gas analysis, Fainberg spent the last years of his life as a scientific instructor in one of the divisions of the Ministry of Chemical Industry.

His erudition and energy were manifested in his all-round scientific activity. Apart from his main work, he lectured on automatics to workers of the Ural factories, and acted as a consultant in the Laboratory of Automatization of the Ukrainian State Institute of Applied Chemistry and in the Institute of Automatics and Telemechanics in the USSR Academy of Sciences.

His textbook on "Automatic Gas Analyzers" is the only work in Russian on this question.

His work in the field of automatic control gained him wide popularity and his activity as an inventor resulted in the introduction of new methods and apparatus into automatic control for our industries. The majority of his 25 inventions are used in industry.

Some of his inventions which are used industrially are: a portable gas analyzer for determination of fuel gas; an apparatus for continuous analyses of fuel gas; a thermochemical gas analyzer for automatic determination of oxygen in fuel and inert gas; an electrochemical gas analyzer for automatic determination of sulfur dioxide; an apparatus for automatic determination of traces of oxygen in gases; etc.

While maintaining a close connection with industrial workers, Fainberg at the same time paid considerable attention to the popularization and clarification of questions of automatic control, and published more than thirty papers in the course of his work.

In 1943 Fainberg was awarded the degree of Candidate of Chemical Sciences.

The fruitful scientific activity of Fainberg was marked by high Government awards. In 1942 he was awarded a Stalin prize and in 1942 the Order of the Red Banner of Labor.

In the person of Mikhail Maksimovich Fainberg the Commission on Analytical Chemistry of the USSR Academy of Sciences, of which he was an active member, has suffered a grievous loss.

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RESOLUTIONS OF THE CONFERENCE ON CLASSICAL METHODS OF CHEMICAL ANALYSIS IN THE GEOCHEM INSTITUTE OF THE USSR ACADEMY OF SCIENCES, HELD IN MOSCOW ON THE 14-17TH OF NOVEMBER 1951

Russia is the birthplace of new paths in analytical chemistry, where both the classical methods of chemical analysis and its theoretical bases have been developed. This indisputable fact is deliberately belittled by foreign scientists. Some of them indulge in direct falsification of the history of chemistry in our country so as to deny the priority of our scientists.

The brilliant investigations of M. V. Lomonosov laid the foundation of chemical analysis just like those of D.I.Mendeleev and A.M.Butlerov, who by their work created an epoch in the development of world science, and strengthened the theoretical basis of analytical chemistry, leading to a wide generalization and the creation of new paths.

To such paths created by our fellow countrymen belong: the development and application of organic reagents in chemical analysis (M.A.Ilinsky and L.A.Chugaev); the development of physico-chemical analysis (N.S. Kurnakov); chromatographic analysis (M.S.Tsvet); microcrystalline analysis (M.V.Lomonosov, T.E.Lovits); crystallo-optical analysis (E.M.Fedorov); spot tests and special tests for metals and alloys (N.A.Tananaev), etc.; N.A.Menshutkin produced the first classical textbook on analytical chemistry.

A new era in analytical chemistry developed after the October Revolution. Thanks to the concern of the Bolshevik Party, the Soviet Government and of Comrade Stalin personally, a turbulent growth of scientific investigation, in factory and university chemical laboratories started. Reagent chemistry has become an industry in itself; general laboratory and precision apparatus are being produced and large numbers of books and journals on analytical chemistry are being published; conferences and meetings devoted to this branch of knowledge are regularly held; a firm link has been established between theory and practice, while the development of the theory and practice of analytical chemistry has attracted large collectives. Soviet analysts actively participate in the building of Communism and help its constructions.

Soviet analytical chemistry which develops on the basis of Marxist-Leninist methodology and endeavors to bring contemporary analytical methods to bear on the problems which face our Socialist constructions, has attained important successes and occupies a leading place in world analytical chemistry.

The Conference on Classical Methods of Analysis, convened by the Commission on Analytical Chemistry of the Geochem Institute at Moscow was marked by the intense activity of the participants. Reports were read which reflect the different approaches in the development of contemporary analytical chemistry. Delegates from 29 cities in the USSR were present including those from Leningrad, Kiev, Saratov, Alma-Ata, Ivanov, Gorky, Kharkov, Lvov, etc.

It was noted at the conference that Soviet chemical analysts have attained considerable success in a number of fields, e.g. the application of the physico-chemical analysis of N.S.Kurnakov to the solution of analytical problems; the study of ionic equilibrium; the application of ionic energetics; the development of the theory of the action of organic reagents, their wide study and use in

inorganic analysis; the study of oxidation-reduction processes, etc.

Particular attention was paid to the question of anomalous separation of elements, especially the phenomenon of coprecipitation.

Systematic studies are being carried out on the study of complex compounds and their application for developing new analytical methods.

A number of investigations devoted to the establishment of regularities in ionic reactions in connection with Mendeleev's periodic law should be noted.

A series of successes has been attained in working out new methods of volumetric and gravimetric analyses and improving those already in use, in the development of micro and semi-micro methods, and in the application of ion exchange in the development and improvement of electroanalytical methods, etc.

New methods of making weights have been worked out, in particular by the application of the inverse link method.

At the same time the conference made a note of a number of deficiencies.

The most important are the following: insufficient further development of new developments in the field of gravimetric, volumetric and electrical methods of analysis, in the field of work on the separation of elements by extraction and absorption methods, and in precipitation by organic reagents, particularly the use of complex-compound formers which act selectively; the slow introduction of new oxidation-reduction and other indicators; the lag in adoption and use of a number of theoretical principles in analytical chemistry developed by Soviet scientists. The analysis of organic materials is weakly developed. Little attention has been given to working out the methods of "phase" analysis of mixtures and the determination of elements of different valencies when they occur together.

The output of weights for macroanalysis is insufficient. The output of semi-micro and micro weights is insufficient to satisfy the increasing demands of scientific-investigational and factory laboratories.

The necessary amount of general laboratory apparatus for semi-micro and micro analysis is not forthcoming; this hinders the development and introduction of new analytical methods into laboratory practice.

The decrease in the number of hours set apart by educational institutions for teaching analytical chemistry, lowers the general standard of scientific training of chemists. The training of average analytical personnel-laboratory workers and preparators in a number of branches of industry is completely unsatisfactory.

The low rate of publication of books on different theoretical and practical questions in analytical chemistry and of journals leads to a considerable delay in the publication of work, including work connected with the priority of Soviet scientists.

The coordination of the work of analysts and its application to the great schemes of Communism is still weak. Work on the unification and standardization of methods of technical analysis has slowed down considerably and in some cases stopped completely. This leads to a considerable difference between the scientific-experimental level of these methods and the contemporary possibilities of analytical chemistry, and this is reflected in the state of the control of production.

The conference regards it necessary to recommend the following measures:

1. To continue to strengthen the link between scientific workers in analyt-

ical chemistry with production, with special reference to increasing the help to the great constructions of Communism, and coordinating the work of different institutions in this field. To ask the Division of Chemical Science of the Academy of Sciences USSR to consider this question and to issue the necessary recommendations.

2) To call regional conferences to attract workers from factory laboratories in order that new methods of analysis can be introduced into factory practice and to generalize the experience of Stakhanovite methods of work.

3) To regard it a necessity to strengthen the links between the Commission on Analytical Chemistry with outlying districts by participation of the Commission in regional meetings and holding All Union meetings not only in Moscow but in other cities also.

4) To ask the Commission to bring about the coordination of scientific work on analytical chemistry carried out in different scientific institutions in the Soviet Union.

5) In the development of the theory and practice of classical methods of analysis, the conference deems it necessary

a) to direct attention to the development of work on the theory of solutions and the solubility of precipitates as applied to analytical chemistry; and to the expediency of holding a special meeting for discussion of these questions

b) to recommend further continuation and expansion of theoretical work along the directions indicated at the present conference; in particular, the application of physico-chemical methods of analysis to the study of systems which are important analytically; the phenomenon of coprecipitation; the thermodynamics of analytical reactions; the application of the periodic law to the fundamental characteristics of ions; the study of organic reagents and their application in analytical chemistry; oxidation-reduction reactions and complex formation; the application of ionites (cationic and anionic exchange resins); new methods of volumetric analysis; group analysis and other rapid methods; electrolysis with the mercury cathode; and the use of statistical methods in evaluating analytical results.

6) In connection with the continuously mounting importance of organic reagents in analysis and the absence at the present time of systematic information about new reagents, as a result of which valuable new reagents do not come into general use for a long time, the conference regards it essential:

to organize within the Commission on Analytical Chemistry a special section for new analytical reagents which, with the participation of the All Union Scientific-Experimental Institute of Chemical Reagents, will consider the value of all the new reagents described, and publish its opinion and its recommendations regarding these reagents.

7) To deem it necessary to hold systematic reviews of the unification and standardization of technical analytical methods with the widespread use of the experience of factory laboratories and research institutes.

8) To continue and expand work on the history of analytical chemistry in our country, to expose foreign scientists engaged in falsification in this connection. To accelerate the publication of monographs on the history of analytical chemistry.

9) To deem it necessary to publish monographs on different topics in analytical chemistry such as: the application of physico-chemical analysis to analytical chemistry; the theory of the action and application of organic rea-

gents; the methods of mathematical statistics in analysis; and thematic collections on special topics in analytical chemistry.

10) To regard it as urgent to increase considerably in the near future the size of the Journal of Analytical Chemistry, because of the hold up in publishing work which often leads to loss of priority for Soviet analysts and hinders the introduction of new and improved methods of analysis in industry.

11) To regard as a necessity the renewal of the publication of chemical reference journals together with a general improvement and increase in annotated bibliographic work with indexes to work in analytical chemistry, printed in different collections.

12) To ask the Ministry of Higher Education to increase the amount of time devoted to teaching analytical chemistry and to reissue a number of books in analytical chemistry.

13) To direct the attention of the Ministry of Machine and Apparatus Construction to the unsatisfactory position which exists with regard to the output of analytical weights, including the application of return communication, particularly for micro and semi-micro analysis.

To ask the Ministry of Machine and Apparatus Construction to suggest to organizations who supply microweights and other apparatus, that they establish closer contact with the Commission on Analytical Chemistry at the Geochem Institute of the USSR Academy of Sciences and not to issue new models of weights without the approval of this Commission.

To organize the preparation of new ion exchange resins.

14) To ask the Ministry of Chemical Industry to expand the production of chemical apparatus and reagents already in use, and also to familiarize the issue of new reagents by lists, approved by the Commission on Analytical Chemistry.

15) To deem it necessary to call a conference on the application of marked atoms; on the chemical side of spectral analysis; the application of organic reagents; on the polarographic and chromatographic methods; the analysis of organic compounds; and also on rapid and automatic methods.

16) To consider the state of terminology in analytical chemistry and to draw up the necessary recommendations.

17) To consider it essential to call a second All Union Conference on Analytical Chemistry soon.

18) To publish the material of the present conference in the form of a separate thematic collection "Work of the Commission of Analytical Chemistry"; to publish the resolutions of the conference in the next numbers of the "Journal of Analytical Chemistry."

A. K. Babko and A. T. Pilipenko, "COLORIMETRIC ANALYSIS".
State Chemical Press, Moscow-Leningrad 1951, 408 pp. Price 20 rubles.

A. K. Babko and A. T. Pilipenko's textbook on colorimetric analysis is one of the first books planned for publication from a series of Russian monographs and manuals on analytical chemistry. This book, which has appeared at a very opportune moment, was designed to fill a serious gap in our literature on colorimetric analysis. In its makeup the book is original and new.

The book is divided into three parts.

The first part is devoted to description and consideration of the conditions necessary for converting the component to be determined into a colored compound. The general laws of light absorption by colored solutions are considered. A considerable amount of information regarding Beer's law, the effect of pH on colorimetric determinations, and the colorimetric determination of complex mixtures is adduced. A section is included here on extraction, in which the extractive separation of the elements is described, apparently in more detail than in any previous textbook on analytical chemistry. The valuable contributions of Babko himself on the deviations from Beer's law are included here as well as his work on the influence of pH on the color, and the ionic composition in solution, etc. On reading this part one feels the easy approach of the authors to the questions of the calculations of different constants, equilibrium ionic concentrations, etc.

In its abundance of theoretical material and depth of approach, the first part of this book is better than the corresponding section of any other textbook on analytical chemistry.

The second part is devoted to consideration of the methods of measuring color intensity and the requisite apparatus. Here, in addition to test methods, the construction and method of operating the visual and photoelectric colorimeters as used in many laboratories are treated in sufficient detail. A special chapter is devoted to the colorimetric determination of mixtures of two colored components.

The third and longest part, which occupies more than half the book, contains descriptions of special methods of colorimetric determination. The material is arranged not according to elements, but in chapters (13 headings) which describe the determination of elements forming related colored compounds. The following groupings are employed: thiocyanate and halogen complexes; the use of NH_3 and organic bases; peroxide compounds; determination of F by weakening of the color; heteropolyacids; inner complex compounds; compounds with dyes containing OH-groups, with organic reagents containing N_2, with organic reagents containing SH groups; methods based on oxidation-reduction methods; the syntheses of organic colored compounds, and methods of determination of pH.

Although we are not happy with regard to the choice of the groups and the relation of the different methods, particularly those connected with the application of organic reagents, to one group or another, we must admit that such a scheme, of course, is more convenient than the method of arrangement according to elements as used in other textbooks. By means of this group arrangement the mechanism of a reaction as well as its selectiveness is emphasized more clearly and results in a greater economy of printing space.

In each chapter separate descriptions are given of the determination of individual elements. Each description is made up on the same model. First, a general description is given which includes information on the theory or idea of

a reaction, and indicates the factors which interfere with the reaction and gives the method of measuring the color and the sensitivity of the reaction. Further, a fairly detailed description is given which includes a brief description of the method, a list of the necessary reagents, and the procedure. Several procedural methods are given for each element; for determinations of the element in pure solutions and in different materials. The literature references are given as footnotes.

By holding strictly to this method of description the book is suitable for use and gives a pleasant impression.

The book is well written, in simple and clear language. It gives the impression of being a reliable textbook, carefully compiled on a strictly scientific basis with due regard to practical considerations.

Although we have thus far given a good review of this book, there are nevertheless some debatable points both of a general and particular character which it is necessary to observe.

In agreeing to write a book on colorimetric analysis in such a small volume (400 pages) the authors took on a thankless task. To give anything like a complete coverage to a subject which is expanding so rapidly at the present time in such a small book is obviously impossible. Therefore the authors had to resort to selection of material which they thought to be of the greatest interest. Naturally different opinions exist with regard to the best selection; e.g. it is not clear why the authors omitted the very useful diethyldithiocarbamate method of estimating Cu while they included the rather insensitive dimethylglyoximepyridine method which necessitates the use of silver nitrate and is a method in which many metals as well as chlorides interfere.

In some places references are made to other methods for the determination of various elements which are not described, but references to the best variants of these other methods are not always given. The question of how to find these best methods in the literature therefore arises.

Colorimetric methods of determining S, Sn, Br, I, Ag, Ca, Cd, Na and a large number of the so-called "rare" elements, Zr, B and others are not described. It would be useful if the authors in their preface explained their motives for choosing the elements and the methods of determining them as they have.

All the textbook, as the authors themselves observed in the preface, is compiled on the basis of Russian literature only. Throughout the book there are only 14 references to the works of foreign scientists. The motives here are not clear either. If good, reliable colorimetric methods for the determination of any element are described in foreign literature, it is not clear why they should not be included in this book.

The authors' views on the influence of pH, and on the conditions of formation of complexes between the different elements and organic reagents which are weak acids (salicylic acid, etc) are very debatable. In this connection the authors almost without reservation show a one-sided approach in which they assume that the conditions for the existence and the formation of complexes are determined solely by the concentration of the anions of the corresponding weak acids, which can be easily calculated on the basis of the dissociation constants of these acids. The nature of the cations, the effect of pH on the state of the cations and other factors relating to the elements are not considered (pp. 60, 64, 72, 161, 166, 240, 295).

When such an approach is used it is possible to reach an unexpected conclu-

sion, that apart from the dependence on the nature of the element, the complexes formed by the element are less stable, the higher the acidity, since according to the increase in acidity the concentration of the complex-forming compound decreases. This is approximately what the authors found (pp. 60, 166 and particularly 240, 295).

In this connection also the authors are faced with the difficulty of explaining the precipitation of elements of the 5th group by H_2S only from strongly acid solutions, in which the concentration of the anions SH^- and $S^{=}$ are very small; of explaining the high stability to acids of the salicylate complexes of Cr^{III}, which is considerably greater than that of the corresponding complexes of Al; or of explaining the capacity of B or Ge to form complexes with hydroxyanthraquinone in concentrated acid media. This one-sided approach of the authors is even more difficult to understand, when there exist works which are undoubtedly known to the authors (e.g. articles in the Journal of Analytic Chemistry, 2, 67 (1947); and the Journal of General Chemistry, 20, 807, 816 (1950)[1]) in which the unequal effect of pH on the capacity of an element to form complexes according to the nature of the element has been clearly demonstrated.

It is of course impossible to include all the methods of colorimetric analysis in such a small book. The authors should immediately undertake a second, considerably expanded edition of their textbook, in which they can eliminate errors which have crept in, and include any useful material left out of the first edition. We wish them luck.

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[1]) See Consultants Bureau English translation, pp. 845, 853.

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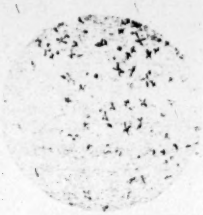
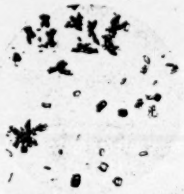
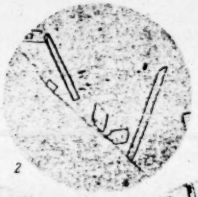


THIOUREA COMPLEXES OF LOW SOLUBILITY AND THEIR APPLICATION IN ANALYSIS
(p. 45 ff.) (Magnified 50 times)

1) $[Bi(CSN_2H_4)_6][Cr(NH_3)_2(CNS)_4]_3$; 2) $[Hg(CSN_2H_4)_4](C_6H_2N_3O_7)_2$;
3) $[Cd(CSN_2H_4)_4](C_6H_2N_3O_7)_2$; 4) $[Cd(CSN_2H_4)_4][Cr(NH_3)_2(CNS)_4]_2$;
5) $[Pb(CSN_2H_4)_4](C_6H_2N_3O_7)_2$; 6) $[Tl(CSN_2H_4)]_x(C_6H_2N_3O_7)$;
7) $[Ag(CSN_2H_4)_2](C_6H_2N_3O_7)$; 8) $[Ag(CSN_2H_4)_2][(CO(NH_3)_2(MO_2)_4]$;
9) $[Cu(CSN_2H_4)_3](C_6H_2N_3O_7)$





MICROCRYSTALLOSCOPIC REACTIONS

FOR NITRATES AND NITRITES (p. 55 ff)

1) 1,4-Aminophenylmercurinitrate.
2) 1,4-Aminophenylmercuriacetate.
3) Nitrosoamine with 1,4-methylaminophenylmercuriacetate.
4) Nitrosoamine with 1,4-ethylaminophenylmercuriacetate.
5) Quinolinemercurinitrite.

Magnified 100 times

NEW REAGENTS

Three new, highly sensitive reagents have been synthesized by the All Union Scientific Experimental Institute of Chemical Reagents.

1) for aluminum ("Stilbazo")

2) for bivalent manganese ("manganon")

3) for bivalent nickel ("nikilon")

Organizations wishing to test the new reagents can obtain samples and instructions for their use on application to the Institute.

Any requests should be sent as soon as possible in order that an idea may be obtained as to how much it is necessary to produce.

THE QUANTITATIVE DETERMINATION OF HALOGEN-ORGANIC COMPOUNDS OF THE ALIPHATIC SERIES

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The most frequently used method for determining the halogen compounds of the aliphatic series is alkaline saponification. The respective inorganic halide thus formed is then determined by one of the usual methods.

The saponification reaction is not always quantitative and depends on many factors [1-5].

Experiments which we carried out on the saponification of different alkyl halides by means of 0.5 N alcoholic KOH in which the reaction mixture was heated on a water bath for 6-8 hours, confirmed that when these normal conditions of saponification are used, the reaction is not quantitative for many compounds. Some examples are given in Table 1.

TABLE 1

Saponification with 0.5 N alcoholic KOH for 6-8 hrs on a water bath[1)]

No.	Halide tested	g	Ml of 0.1 N $AgNO_3$ used	Halogen Found %	Halogen Computed %
1	Butyl chloride	0.1674 0.1461	8.28 6.29	17.54 15.27	38.35
2	Allyl bromide	0.2184 0.2240	16.00 16.42	58.55 58.58	66.12
3	Ethylene bromide	0.5140 0.6330	36.77 44.84	57.17 56.61	85.09

[1)] For other examples see V. S. Letina's work on "Methods for the quantitative determination of halogens in organic compounds by the action of the alkaline metals in an indifferent solvent". Moscow. All-Union Scientific- Research Chemico-Pharmaceutical Institute, (1947).

The use of high pressures (sealed tubes) in many cases leads to quantitative results. In this connection we carried out some experiments on the alkaline saponification of aliphatic halides in which an autoclave was used, in order to standardize the method of estimation. We used a rotating autoclave made of stainless steel with a capacity of 250 ml. In the first experiments the test

sample was placed in the autoclave with 0.5 N alcoholic KOH, the autoclave was set in motion and was heated externally by means of a burner. The internal temperature was held at 100° for 1 hour. The contents of the autoclave were then transferred into a conical flask and the halogen determined either by Volhard's method or potentiometrically.

For a number of halogen derivatives even these conditions were insufficient; the results obtained were low. Thus dichloroethane only gave 54.79% Cl; CCl_4 – 68.37%; and CH_2Cl_2 21.9%.

After further modifications of the temperature and the reaction medium we got results for different halides which agreed with theory. Saponification was carried out in the autoclave with a mixture of 0.5 N alcoholic KOH and 10% aqueous alkali for 1 hour at 200°. The results are given in Table 2.

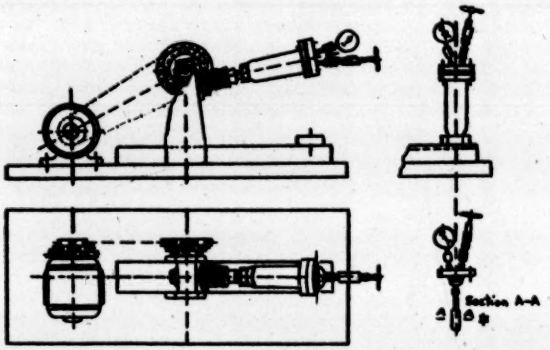
TABLE 2

No.	Compound analyzed	g	Ml of 0.1 N $AgNO_3$ used	Halogen Obtained %	Halogen Computed %	Recovery %
1	Butyl chloride	0.1286 0.1374	13.84 14.79	38.16 38.16	38.35	99.5
2	Methylene chloride . . .	0.1545	36.07	82.79	83.50	99.15
3	Dichloroethane	0.1778	35.57	70.94	71.67	98.99
4	Chloroform	0.1519	37.85	88.36	89.10	99.17
5	Carbon tetrachloride . .	0.1281	32.78	90.74	92.19	98.43
6	Hexachloroethane	0.1005	24.94	88.00	89.86	(Carius 87.98)
7	Ethylchloroformate . . .	0.2792	24.19	30.72	32.70	(Carius 30.69)
8	Dichloroacetic acid . .	0.1330 0.1383	20.46 21.28	54.55 54.56	55.01	99.1
9	Trichloroacetic acid . .	0.1281 0.1305	23.28 23.86	64.44 64.83	65.11	99.5
10	Chloretone	0.2020	32.36	56.81	56.47	100.60
11	Diethylaminoethylchloride	0.1617	11.90	26.10	26.1	100.0
12	Allyl bromide	0.1878 0.1608	15.54 13.29	66.13 66.11	66.12	100.0
13	Ethyl bromide	0.4800	48.50	72.43	73.3	98.81
14	Butyl bromide	0.4630 0.1701 0.1640	33.78 12.39 11.96	58.31 58.21 58.32	58.31	100.0
15	Ethylene bromide	0.1965 0.2504	20.93 26.73	85.13 85.31	85.09	100.04
16	Methyl iodide	0.3048 0.2600	21.50 18.36	89.52 89.62	89.43	100.10
17	Ethyl iodide	0.2524 0.2123	16.11 13.60	81.01 81.30	81.43	99.84
18	Iodoform	0.3182	24.28	96.84	96.69	100.15
19	Bromocamphor	0.2009	8.6	34.21	34.63	98.79

This table shows that recovery of the halogens under these conditions is complete and the method is of general application; (Cl, Br, I) are broken off from polyhalides and highly volatile compounds.

The method is very simple and only requires 2 hours for completion. In the course of the last 2 years we have used it for the determination of halogens in aliphatic compounds and have confirmed the results by means of the Carius method, with which we got good agreement.

The autoclave used is available; we got one from the Chemico-Analytical Laboratory of the Mendeleev All-Union Chemical Society (see diagram) but it can be made in any well equipped mechanical workshop.



Rotating autoclave

Description of the Method for the Determination of Halogens in Aliphatic Compounds

0.15–0.3 g (accurately weighed) of the test material is placed in a round thin-walled ampoule, the end of which is then sealed off. 20 ml of 0.5 N alcoholic KOH and 15 ml of 10% aqueous NaOH are placed in the autoclave. The end of the ampoule is broken off and placed together with it in the autoclave. The lid of the autoclave is hermetically sealed on and the apparatus set in rotation. It is heated externally for 1 hour. The temperature is maintained at ~200° (the thermometer is fixed in a case fitted to the autoclave). After cooling the excess pressure is released from the autoclave and the lid unscrewed. The contents are transferred quantitatively to a conical flask, and the halogens are then determined either by Volhard's method or potentiometrically.

If the test sample is solid, then it can be weighed in a boat; if it is a very volatile liquid, then the end of the glass ampoule should not be broken off before placing it in the autoclave, since it will be broken during rotation by the blades leading from the autoclave lid into the cup (the blades are made for the efficient stirring of the contents).

SUMMARY

A method is described for the quantitative determination of halogens in aliphatic halogen compounds (Cl, Br, I) by saponification with alcoholic-aqueous alkali in an autoclave maintained at 200° for 1 hour.

Received January 14, 1952

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THE QUANTITATIVE COLORIMETRIC DETERMINATION OF EPIHYDRIN ALDEHYDE FORMED DURING THE OXIDATION OF FATS

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In the investigation of the oxidative break down of fats and fatty acids, the initial phase of this process which precedes the manifestation of organoleptic signs of break down is of particular importance. The determination of epihydrin aldehyde, which as we have shown in our own researches in particular, is one of the products characteristic of the first stages of oxidative changes in fat, is of vital importance in the methods employed for the study of the initial changes in fats which are subject to autoxidation.

Epihydrin aldehyde is determined in fats either qualitatively or in some instances approximately quantitatively by the development of a red color in the Kreis reaction [1].

Since Powick [2] and later Pritzker and Jungkunz [3] established that the reason for the development of a red color in the Kreis reaction for oxidized fats is the presence of epihydrin aldehyde in them, this reaction can be considered as specific for epihydrin aldehyde and consequently can be used for its quantitative determination. This characteristic of the Kreis reaction is not changed significantly, even if the opinion expressed in one of our investigations [4] is accepted, that in some instances the Kreis reaction is the result of, to some extent, the presence of higher homologs of epihydrin aldehyde in the oxidized fat.

Several investigations are noted in the literature in which attempts have been made to give a quantitative evaluation of the color which develops in the Kreis reaction, or to use this color for the quantitative determination of epihydrin aldehyde in fats. Holm and Greenbank [5] first proposed the use of acid solutions of methyred for approximate evaluation of the intensity of the color. Later a similar colorimetric method for the approximate evaluation of the intensity of the color developed in the Kreis reaction was described by Pritzker and Jungkunz [6] in which a solution of 1.2 mg of $KMnO_4$ in 100 ml H_2O was proposed as the solution for comparison. A more exact method of evaluating the intensity of the color of the reaction for ipihydrin aldehyde was the use of Lovibond red units, which was that adopted in Aas' method [7]. He established a linear relation between color intensity and the concentration of the colored reaction product.

A more detailed method for the determination of epihydrin aldehyde was studied by Taufel and Russow [8] who by means of epihydrin aldehyde which they synthesized, worked out a method for an approximate colorimetric determination with a standard color scale prepared from solutions of methyl red and permanganate. In a later publication Taufel and Seuss [9] proposed a scale which approximates closely to the colors of the Kreis reaction. This scale was prepared by the dilution of a 0.1% aqueous solution of acid fuchsin with acidified water.

All the methods which have been mentioned only given an approximately quantitative expression for the determination of epihydrin aldehyde. Only in Pyke's [10] work was the relation between the color intensity as measured by means of red Lovibond filters, and the concentration of epihydrin aldehyde investigated. This was expressed by the formula

$$\text{Red Lovibond units} = 97\ (C_3H_4O_2\%) + 0.625$$

and in this way indicated a more accurate method for the colorimetric determination of epihydrin aldehyde.

It should be noted, that different methods of carrying out the Kreis reaction itself are given in all the references cited. This can be explained by the difficulties which arise in attempting to use the color of a reaction for quantitative and semiquantitative determinations, and is connected with the choice of color scale and choice of method for carrying out the colorimetric determination, and also with the method of realizing the Kreis reaction itself. The intensity of the color in the Kreis reaction depends not only on the quality, and ratios of the reactants in the reaction mixture, but also on the temperature and reaction time.

In addition, in some instances when the color reaction is carried out, fine emulsions or supplementary colors can be formed in the colored layer, the presence of which interferes with exact colorimetric determination. This fact compelled Tauffel and Seuss in the work already cited, instead of carrying out the usual method for the reaction, to use a preliminary distillation of the epihydrin aldehyde in a stream of air; the distilled aldehyde was then trapped in a mixture of equal parts of 1% solution of phloroglucinol in alcohol, and concentrated sulfuric acid. In order to accomplish this a special apparatus described by Tauffel and Sadler [11] is necessary. In addition a number of precautions must be taken, which nevertheless do not guarantee freedom from errors connected with possible losses of epihydrin aldehyde as a result of incomplete absorption, or further oxidation by atmospheric oxygen. All these drawbacks deprive the roundabout distillation method of any advantages it has over the usual method of carrying out the reaction.

In an attempt to work out a method for the determination of epihydrin aldehyde which is not only reliable enough but is also simple and can be carried out in any laboratory, we left out the distillation method which is lengthy and unreliable and necessitates the use of special apparatus, and instead concentrated on the usual technique for carrying out the color reaction. Such a method in which certain conditions are observed, at least for the vast majority of fats and fatty acids, does not lead to any appreciable deviations in the intensity of the color developed, which might affect the results. We established that if a solution of 1 ml of the test fat in 2 ml of ether is mixed with 1 ml 37% chemically pure HCl, and shaken up, followed by the addition of 2 ml of a 0.1% solution of phloroglucinol in ether, and the final mixture again shaken and heated for 1 minute at 100°, a color develops in the lower aqueous layer the volume of which is 2 ml. This color attains a maximum in 1 minute, after which it remains fairly constant for some time, and then begins to weaken or changes its character. Thus a colorimetric determination can be carried out under these conditions 2 minutes after mixing the reagents.

Further, in contrast to Pyke we found that the relation between color intensity as measured by Lovibond red units and the concentration of epihydrin aldehyde solutions was expressed more closely by the formula:

$$\text{Red Lovibond units} = 100\ (C_3H_4O_2\%) + 0.60.$$

In order to simplify as much as possible the colorimetric part of the determination, we made up a series of standard colored liquids. Colorimetric determination is thus carried out by simple comparison by means of a comparator of the colors developed in the Kreis reaction with standard colors. We used acid fuchsin for the preparation of these standards, since acid fuchsin solutions are the only ones of all the colored solutions proposed for this purpose, which have colors practically identical with that developed in the epihydrin aldehyde reaction. The preparation of a color scale is very simple and is accomplished by dilution to a range of concentrations of a stock 1% aqueous solution of acid fuchsin with distilled water, 1000 ml of which contains approximately 0.5 ml 20% sulfuric acid. The colors of the solutions obtained are sufficiently stable if they are kept in sealed or well stoppered test tubes. The intensity of the colors hardly changes at all in the course of four months if protected from the action of direct or very intense diffuse solar light.

The volumes of a 0.1% solution of fuchsin in ml necessary to prepare standard solutions by making up to a volume of 50 ml with water are given in the table below. In addition, the intensities of the colors measured in red Lovibond units and the corresponding concentrations of epihydrin aldehyde are included.

No.	Vols. of 0.1% fuchsin solution in ml to be made up to 50 ml with acidified water	Color intensity (Red Lovibond units)	Mg of epihydrin aldehyde in 1 ml of liquid
1	0.05	0.75	0.015
2	0.1	1.5	0.090
3	0.2	3.0	0.240
4	0.3	4.5	0.390
5	0.4	6.0	0.540
6	0.5	7.5	0.690
7	0.6	9.0	0.840
8	0.7	10.5	0.990
9	0.8	12.0	1.140
10	0.9	13.0	1.240

Such a scale is sufficiently accurate for normal practical determination of epihydrin aldehyde. If it is required to increase the accuracy, intermediate standards can be prepared at different parts of the scale, so that the scale can be supplemented with standard solutions, for which, by simple interpolation it is easy to find the value of the corresponding concentration of epihydrin aldehyde. It should be remembered that the accuracy of the determination depends on a number of factors; the accuracy of the measurement of the volume of the liquid being colorimetrically determined, the stability of the reaction colors, the influence of temperature and other factors.

The method adopted was briefly as follows:

An accurately weighed aliquot of ~1 g of the test fat or fatty acid is placed in a graduated flask of colorless glass fitted with a ground glass stopper of the same size as the flask, and dissolved in 2 ml of ether. 1 ml of 37% chemically pure HCl is added and the mixture shaken. 2 ml of a 0.1% solution of phloroglucinol in ether is then added and the whole shaken again after which it is

placed on a boiling water bath for 1 minute. The test tube is withdrawn from the bath and after 1 minute the color of the lower layer is compared with the standards in a comparator. The determination should occupy in all only 10 minutes. The volume of colored layer is measured, and from the value found for the concentration of epihydrin aldehyde and the volume of the colored liquid the content of epihydrin aldehyde in the aliquot taken, or in 100 g of the test fat, is calculated.

The color reaction with phloroglucinol is very sensitive; by means of it 0.0005 mg of epihydrin aldehyde in 1 ml can be detected. If resorcinol or naphthoresorcinol are substituted for phloroglucinol the sensitivity decreases. Thus, when resorcinol is used, the limiting concentration of aldehyde which can be detected by the development of a color is 0.01 mg/ml.

The method described for the determination of epihydrin aldehyde gives good concurrent results for the majority of fats and fatty acids which are in the initial stages of autoxidation. The method however is not applicable to fats which have an intense inherent color, or to fats and fatty acids containing additives which give colors with the reagents used in the colorimetric determination, or for cases of strongly oxidized fats for which the content of epihydrin aldehyde is not a true indication of the break down.

SUMMARY

A simple method is described for the quantitative colorimetric determination of epihydrin aldehyde formed during the oxidation of fats and fatty acids. The method is based on the formation of colors in the Kreis reaction. The method described can be used in any laboratory and enables the determination to be carried out in 10 minutes with an accuracy which is satisfactory for most practical purposes.

The factors which affect the results are pointed out, as well as the cases in which the colorimetric method described is inapplicable.

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THE QUANTITATIVE DETERMINATION OF THE DEHYDRATION OF CERTAIN ALCOHOLS

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It has been established [1,2,3] that the process of catalytic dehydration of certain alcohols followsa well defined path, i.e. water and the corresponding hydrocarbon are formed.

When it is necessary to control the reaction, particularly if dehydration is being studied in a stream of gas, it is very important to follow the path of the process not only by the amount of gas formed, but also by the amount of water formed. The latter can easily be tracked if the original material is mixed with water in any ratio, and the binary aqueous-alcohol mixture possesses some property which is simply related to the quantitative ratios of the components. We have shown in our investigations that the refractive index is such a property for ethyl and propyl alcohols, this being especially true for mixtures containing 40-60 mol% water and more.

In a simple process the degree of dehydration is linearly dependent on the gas which is formed, while the relation between dehydration and the refractive index is more complex; the refractive index n of a two component mixture is related to the density d which is variable, by one of the following relations

$$\frac{n-1}{d} = \text{const}, \quad \frac{n^2-1}{d} = \text{const} \quad \text{and} \quad \frac{1}{d}\,\frac{n^2-1}{n^2+2} = \text{const}$$

which can afterwards be related to the refractive indices of the components and their content in percentage weight. More details are given in the works of Pavlov [4], Doroshevsky [5], and others. Nevertheless, the practical application of the relations given above is complicated, as a result of the introduction of correction factors and the complexity of the calculations.

The aim of this present work, while not dwelling on the theory of this important and interesting question, is to give a possible quantitative method for the determination of dehydration by means of the refractive index on the basis of the tables given below, which were compiled from the results of careful measurements.

As investigations [5,6] have shown, aqueous solutions of the alcohols examined have a maximum for the refractive index, which is observed at 15-25° in mixtures containing 16-20 wt % or 33-39 mol % of water; 5-6 wt % or 16-18 mol % ethyl alcohol; and 3 wt % or 10 mol % of isopropyl alcohol. According to our work (vide tables) the maximum in solutions of ethyl and n-propyl alcohol is approximately the same; while in the isopropyl alcohol the maximum is at 8 mol %.

The accuracy of the results determined by refractive index depends not only on the accuracy of the refractometer itself, but also on the degree of dehydration. For the Abbe refractometer which we used the following accuracies were obtained 1) in the case of ethyl alcohol for 58% dehydration the error does not exceed 0.73%; for 63%-0.47%; for 72% - 0.26%; for 80% - 0.17%; for 85% - 0.1% and for 90% and over not more than 0.07-0.05%.

2) In the case of n-propyl alcohol, for 40% dehydration the error is equal to 0.62%; for 51% - 0.42%; for 65.5% - 0.31%; for 76.6% - 0.11%; over 76.6% - 0.03%.

3) In the case of isopropyl alcohol for 50% dehydration the error is equal to 0.63%; for 60% - 0.31%; for 84% - 0.1%; over 84% down to 0.02%.

Obviously with increasing dehydration the accuracy of determination increases and the error decreases for the propyl alcohols 0.03-0.02%.

The accuracy of the results calculated from the gas depends on the accuracy of the measurement of t°, P and V. If inaccuracies in the measurements of t° and P are neglected, and the volume of gas is measured with an accuracy of 0.5 ml/500 ml, the error in any result will be 0.1%, and only when the volume can be measured with an accuracy of 0.1 ml will the error fall to 0.02%.

Consequently the refractive index method can be successfully used for the quantitative determination of dehydration when the degree of dehydration of the particular alcohol concerned is greater than 50-60%.

Original Materials

The water was twice distilled and its refractive index determined. Doroshevsky's results and others from the Technical Encyclopedia are given for comparison.

	Doroshevsky	Tech.Encyc. Vol.VIII p.42	Our Results
n_D^{15}	1.33339	1.3334	1.3334
n_D^{20}	1.33298	1.3330	1.3330
n_D^{25}	1.33258(n_D^{24})	1.3325	1.3325
d_4^{20}	0.99823		

The alcohols were also twice distilled and the middle fractions taken. They were dehydrated by Doroshevsky's method. His results and those from the Technical Encyclopedia are included for comparison:

1. Ethyl Alcohol

Chemical Handbook, 1948	Tech. Encyl. Vol.V p.159	Doroshevsky
d_4^{20} 0.789	0.78934	0.7886 (22°)
d_4^{25} -	0.78506	0.7851

Our Results	Tech. Encyl Vol.VIII p.79, 45	Doroshevsky
n_D^{15} -	1.36332	1.36230 (17.5°)
n_D^{20} 1.3614	1.36242 (18.35°)	1.36127
n_D^{25} 1.3593	-	1.3594

3. Isopropyl Alcohol

Chemical Handbook, 1948	Tech. Encyl. p 46	Doroshevsky p.130 (Bryul)
d_4^{20} 0.785	0.7887	0.7887

Our Results	Tech. Encyl	Doroshevsky p. 251
n_D^{15} 1.3793	1.3792	1.37922
n_D^{20} 1.3774	1.37757	1.37727
n_D^{25} 1.3755	-	-

2. n-Propyl Alcohol

	Chemical Handbook	Tech. Encycl. Vol. VIII p. 46	Doroshevsky p. 123
d_4^{20}	0.803	0.8044	0.80365
	Our Results	**Tech. Encycl. p. 46, 92**	**Doroshevsky**
n_D^{15}	1.3873	1.38726	1.38729
n_D^{20}	1.3854	1.38543	1.38547

TABLE 1

Dehydration of Ethyl Alcohol According to Refractive Index

No.	Water, wt. %	% Dehydration	n_D^{20}	n_D^{23}	n_D^{25}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
1	Pure Ethyl alcohol	-	1.3614	1.3601	1.3593	4.2
2	0.92	2.32	19	06	98	4.2
3	3.02	7.37	26	13	1.3605	4.2
4	5.27	12.45	32	20	11	4.2
5	8.28	18.76	39	26	18	4.2
6	11.36	24.68	44	32	23	4.2
7	14.95	31.01	47	35	27	4.0
8	20.00	39.00	49	37	29	4.0
9	25.01	46.03	48	36	28	4.0
10	30.04	52.34	45	33	25	4.0
11	35.04	57.97	40	28	20	4.0
12	40.05	63.07	33	21	13	4.0
13	45.07	67.72	23	12	04	3.8
14	50.00	71.89	12	02	1.3595	3.4
15	51.65	73.20	07	1.3597	90	3.4
16	54.07	75.07	00	91	84	3.2
17	55.33	76.00	1.3596	87	80	3.2
18	57.18	77.35	89	80	74	3.0
19	60.65	79.76	78	69	63	3.0
20	61.67	80.45	74	65	59	3.0
21	62.82	81.20	68	59	53	3.0
22	64.39	82.22	61	52	46	3.0
23	65.64	83.01	56	47	41	3.0
24	66.37	83.46	53	44	38	3.0
25	67.29	84.03	48	40	34	2.8
26	68.47	84.74	1.3542	1.3534	1.3528	2.8
27	68.87	84.98	40	32	26	2.8
28	69.75	85.50	35	27	22	2.6
29	70.78	86.11	29	21	16	2.6
30	73.30	87.56	14	07	02	2.4
31	74.76	88.34	06	1.3499	1.3495	2.2
32	77.83	89.97	1.3485	79	75	2.0

(Continued on next page)

Table 1 (continued)

No.	Water, wt. %	% Dehydration	n_D^{20}	n_D^{23}	n_D^{25}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
33	79.46	90.82	73	68	64	1.8
34	82.96	92.57	48	43	40	1.6
35	86.00	94.02	25	21	18	1.4
36	87.56	94.74	13	09	06	1.4
37	90.00	95.84	1.3395	1.3391	1.3388	1.4
38	90.73	96.16	90	86	84	1.2
39	91.65	96.56	83	79	77	1.2
40	93.65	97.24	72	68	66	1.2
41	95.20	98.07	60	56	54	1.2
42	95.77	98.31	57	54	52	1.0
43	97.08	98.84	49	46	44	1.0
44	98.45	99.39	41	38	36	1.0
45	98.63	99.46	40	37	35	1.0
46	98.98	99.58	38	35	33	1.0
47	99.24	99.70	36	33	31	1.0
48	99.57	99.81	34	31	29	1.0
49	99.87	99.95	31	28	26	1.0
50	100	100	30	27	25	1.0

TABLE 2

Dehydration of n-Propyl Alcohol according to Refractive Index

No.	Water, wt. %	% Dehydration	n_D^{15}	n_D^{20}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
1	Pure Propyl alcohol	-	1.3873	1.3854	3.8
2	0.62	2.04	73	55	3.6
3	1.6	5.14	73	55	3.6
4	2.3	7.28	74	55	3.8
5	3.6	11.08	74	55	3.8
6	5.2	15.47	71	53	3.6
7	6.66	19.23	65	47	3.6
8	8.7	24.12	60	42	3.6
9	10.0	27.04	57	39	3.6
10	10.8	28.77	55	37	3.6
11	12.12	31.52	52	34	3.6
12	13.59	34.41	48	30	3.6
13	16.63	39.96	40	22	3.6
14	20.0	45.47	32	14	3.6
15	21.59	47.93	28	10	3.6
16	23.00	49.91	24	06	3.6
17	23.71	50.90	22	04	3.6
18	26.20	54.22	14	1.3796	3.6
19	28.80	57.43	1.3805	88	3.4
20	30.00	58.84	07	84	3.4
21	32.40	61.52	1.3793	76	3.4
22	34.77	64.00	85	68	3.4
23	37.0	66.21	77	60	3.4
24	38.38	67.51	72	55	3.4
25	40.00	68.99	66	50	3.2

Table 2 (continued)

No.	Water, wt. %	% Dehydration	n_D^{15}	n_D^{23}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
26	42.27	70.95	56	40	3.2
27	45.22	73.36	39	23	3.2
28	47.40	75.04	26	10	3.2
29	49.54	76.61	13	1.3698	3.0
30	50.00	76.94	1.3710	1.3695	3.0
31	53.00	79.00	1.3692	77	3.0
32	55.28	80.48	78	64	2.8
33	57.01	81.56	69	55	2.8
34	60.00	83.35	53	40	2.6
35	62.3	84.64	40	27	2.6
36	65.29	86.25	22	09	2.6
37	65.9	86.57	19	06	2.6
38	67.95	87.61	06	1.3594	2.4
39	70.00	88.62	1.3592	80	2.4
40	71.28	89.22	84	72	2.4
41	73.56	90.27	70	58	2.4
42	74.51	90.70	63	52	2.2
43	76.8	91.70	49	38	2.2
44	78.9	92.58	34	24	2.0
45	80.0	93.03	23	14	1.8
46	83.54	94.41	1.3492	1.3484	1.6
47	86.9	95.68	61	54	1.4
48	90	96.78	31	25	1.2
49	90.28	96.87	28	22	1.2
50	91.73	97.37	13	08	1.0
51	95.70	98.67	1.3374	1.3369	1.0
52	97.12	99.12	61	57	0.8
53	97.71	99.30	55	51	0.8
54	98.10	99.42	52	48	0.8
55	98.45	99.53	49	45	0.8
56	98.81	99.64	46	42	0.8
57	99.14	99.74	43	39	0.8
58	99.43	99.83	40	36	0.8
59	99.73	99.92	37	33	0.8
60	100	100	34	30	0.8

TABLE 3

Dehydration of Isopropyl Alcohol According to Refractive Index

No.	Water, wt. %	% Dehydration	n_D^{20}	n_D^{23}	n_D^{25}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
1	Pure Isopropyl alcohol	-	1.3774	1.3763	1.3755	3.8
2	2.51	7.91	76	64	56	4.0
3	3.29	10.19	74	62	54	4.0
4	7.09	20.29	71	58	50	4.2
5	11.57	30.38	68	57	49	3.8
6	16.91	40.43	61	50	42	3.8
7	19.98	45.44	57	46	38	3.8
8	23.39	50.45	51	40	32	3.8
9	27.17	55.44	43	32	25	3.6

Table 3 (continued)

No.	Water, wt. %	% Dehydration	n_D^{20}	n_D^{23}	n_D^{25}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
10	31.41	60.43	32	21	14	3.6
11	33.75	62.95	26	15	08	3.6
12	36.17	65.40	18	07	00	3.6
13	38.82	67.91	09	1.3699	1.3691	3.6
14	41.59	70.37	1.3699	89	82	3.4
15	43.05	71.60	94	84	77	3.4
16	44.58	72.85	88	78	71	3.4
17	46.17	74.10	82	72	65	3.4
18	47.79	75.33	76	66	60	3.2
19	49.50	76.58	70	60	54	3.2
20	51.25	77.81	63	54	48	3.0
21	53.08	79.05	56	47	41	3.0
22	54.96	80.28	49	40	34	3.0
23	56.96	81.53	41	32	26	3.0
24	59.00	82.76	32	23	17	3.0
25	61.15	84.00	1.3622	1.3614	1.3608	2.8
26	63.37	85.23	10	02	1.3597	2.6
27	65.71	86.47	1.3597	1.3589	84	2.6
28	68.11	87.69	82	75	70	2.4
29	70.66	88.93	67	60	56	2.2
30	73.31	90.16	50	44	40	2.0
31	75.54	91.15	35	30	26	1.8
32	77.82	92.13	19	14	11	1.6
33	80.23	93.12	1.3492	1.3497	1.3494	1.6
34	82.70	94.10	84	80	77	1.4
35	85.31	95.09	64	60	57	1.4
36	89.99	96.07	42	38	36	1.2
37	90.82	97.06	18	14	12	1.2
38	92.27	97.55	06	02	00	1.2
39	93.75	98.04	1.3392	1.3388	1.3386	1.2
40	95.26	98.53	79	75	73	1.2
41	96.83	99.02	63	60	58	1.0
42	97.19	99.14	60	57	55	1.0
43	97.74	99.31	55	52	50	1.0
44	98.38	99.51	48	45	43	1.0
45	99.68	99.60	45	42	40	1.0
46	99.14	99.74	41	38	36	1.0
47	99.47	99.84	37	34	32	1.0
48	100	100	30	27	25	1.0

EXPERIMENTAL

The water-alcohol mixtures were prepared by volume and by weight in special flasks fitted with ground glass stoppers with capacities of 12-20 ml for solutions containing water up to 99 mol.% and in 50 ml flasks for more dilute solutions. The solutions were made up a few times and the determinations of the refractive index were also repeated as a check. The temperature of the apparatus was maintained at the necessary level and the refractometer prism washed with water at the same temperature.

The refractive index was determined at 20, 23 and 25° for ethyl alcohol-

water and isopropyl alcohol-water and at 15 and 20° for n-propyl alcohol-water mixtures.

The $\frac{\Delta n}{\Delta t} \cdot 10^4$ column in the tables shows the change of refractive index with a change of 1° in temperature. The results are given in Tables 1, 2 and 3. When no value is given in the table for the refractive index, the percentage dehydration is calculated by interpolation, on the assumption that for small intervals the relationship is linear.

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SUMMARY

1. The relation between percentage composition and the refractive index of binary aqueous-alcohol mixtures has been studied.

2. A refractive index method can be successfully applied to the quantitative determination of the dehydration of certain alcohols, particularly when dehydration is more than 40-60%.

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SPECIFIC REACTIONS AND METHODS IN ORGANIC ANALYSIS

1. THE DETECTION AND QUANTITATIVE DETERMINATION OF TRACES OF PIPERIDINE IN THE PRESENCE OF PYRIDINE

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In recent years a number of more or less successful attempts have been made to apply specific reactions to the analysis of organic compounds. It is obvious that the solution of this question in the contemporary chemistry of organic compounds is of paramount scientific and practical importance; at the same time, the investigator is faced with difficulties, to surmount which is far beyond the limits of possibility for the majority of the corresponding classical methods.

At the present time it is impossible to point out any general approach for the solution of each concrete problem within the present framework of ideas. One of us has shown that in a number of instances good results can be obtained by changing the substance sought and which is present in a mixture with other substances of similar structure, into the corresponding specific reagent, which in turn can be detected by means of a suitable inorganic compound [1].

Naturally this method is not the only possible one; for the solution of the problems indicated, other methods from the arsenal of organic and analytical methods can be applied. In particular, we are convinced that the application of specific complex formation, and the use of reactions as a result of which molecular compounds of the substances sought are formed with inorganic or organic components, will lead to a successful solution.

A multitude of more or less specific reactions for whole classes of compounds possessing functional groups are known in the contemporary chemical analysis of organic compounds; unfortunately these reactions are far from universal, and particularly serious difficulties are encountered when complex multifunctional individuals are dealt with. In addition, the abundance of different organic compounds frequently of similar properties (derivatives of penta and hexa-methylene, pyridine and piperidine etc.), sometimes even belonging to different classes (derivatives of benzene and thiophene, pyrrole, furane, etc.) makes it an essential problem to develop reactions which are not universally specific for a whole class (there are actually no such reactions in organic chemistry), but exhibit a strictly intraclass specificity. Such an approach in the chemical analysis of organic compounds, in the opinion of the authors, has great practical significance.

The present article is devoted to the detection and quantitative determination of piperidine in the presence of pyridine.

While there is a number of characteristic color reactions for pyridine by means of which it can be detected in the presence of piperidine, the solution of the reverse problem (piperidine in the presence of pyridine) is extremely difficult. We could only find one reaction for piperidine in the literature and that was of low specificity – the use of acetaldehyde and sodium nitroprusside [2]. With respect to the quantitative determination of piperidine in the presence

of pyridine, as far as we know[1] only one method, a straight potentiometric method has been described [3]. This method naturally cannot be applied even when the amount of piperidine to pyridine approximates to 1-5%.

Thus, in fact up to the present time there has been no method available for the qualitative detection and quantitative determination of traces of piperidine in the presence of pyridine. Meanwhile the necessity for suitable methods and their scientific and practical importance can scarcely be disputed.

Diltey and Witzingen [4] as long ago as 1926 made a curious observation, re the formation of colorless complex compounds between certain triphenylmethane dyes and piperidine, in contrast to pyridine which does not yield complexes. These observations were confirmed in a further series of investigations by Rumanian workers [5,6] who also established that ammonia behaves in a similar fashion to piperidine. Our work, shows that in addition to piperidine and ammonia, colorless compounds are also formed as the result of interaction between these triphenylmethane dyes and ethylenediamine, and monoethanolamine. Further, we established that a number of other amines and in general organic bases, particularly diisoamylamine, diisobutylamine, isobutylamine, lutidine, isobutylidene, tetramethylpyridine, trimethylpyridine, diethanolamine, triethanolamine, triethanolamine triacetate, monoethanolamine diacetate, and the N-mono acetate of monoethanolamine do not react with these triphenylmethane dyes under similar conditions.

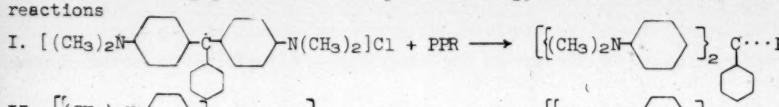
These facts gave grounds for assuming that the interaction of piperidine (PPR) with triphenylmethane dyes proceeds according to the scheme

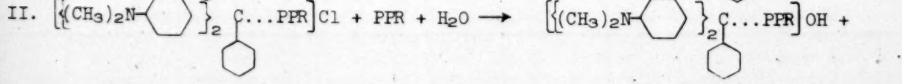
$$\underset{\text{colored}}{[Ar_3C]X} \underset{\text{water}}{\overset{\text{piperidine}}{\rightleftharpoons}} \underset{\text{colorless}}{[Ar_3C\ldots PPR]X}$$

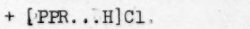
and that the decolorization which accompanies the reaction can be used as the basis for a specific method for the detection and determination of piperidine in the presence of pyridine and its homologs. The interfering action of ammonia, the presenceof which in technical products is not excluded, can be eliminated by known methods.

Triphenylmethane dyes such as crystal violet and fuchsine, form complexes with piperidine which are easily decomposed by water. Water acts similarily with the reaction products of these dyes with ammonia. Malachite green on the other hand reacts with piperidine (but not ammonia) to form a complex compound of the carbinol base type which is stable to water. This fact makes malachite green particularly suitable as a reagent for piperidine (PPR).

Thus as a basis for our proposed method for the detection and quantitative determination of piperidine in the presence of pyridine we have the following reactions

I. 

II. 



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1) In addition there is a brief description of a method for the quantitative determination of piperidine in the presence of pyridine, by converting it into the corresponding dithiocarbonate [7].

The effect of the reaction is decolorization of the malachite green. It should be noted that the proposed method could be successfully used for the detection and determination of monoethanolamine in the presence of its homologs and derivatives, and also of ethylenediamine in the presence of aliphatic amines. The qualitative reaction for piperidine with malachite green is carried out by spot test technique on reagent paper soaked with a solution of the dye. When a drop of pyridine containing piperidine is placed on the reagent paper, formation of a colorless spot occurs in a few seconds or if the concentration of piperidine is low, partial decolorization can be observed. The stability of the spot in air depends on the concentration of piperidine in the test solution. Thus, e.g. for a concentration of 0.1% of piperidine in pyridine, decolorization of the spot can be observed and the white color is completely stable; for piperidine concentrations less than 0.1%, only partial decolorization is observed as compared with a control spot, prepared by the use of piperidine-free pyridine. In this way it is possible to detect piperidine in concentrations not less than 0.05%. Spots, however which have been formed by pyridine solutions of piperidine in concentration of from 0.05 – 0.1% regain a green color on standing for some time.

It is possible therefore to detect 1 μg of piperidine, for a limiting ratio of piperidine to pyridine of 1:2000 (0.05% solution).

The quantitative determination of the piperidine is based on the measurement of the decrease in the light absorption coefficient of the malachite green solution as a result of the effect of test solutions.

As can be seen from Fig. 1 the maximum absorption of a methanol-pyridine solution of malachite green lies near 610 mμ. Consequently, colorimetric measurements must in this case be made in the spectral region, corresponding to the indicated wave length.

A calibration curve is given in Fig. 2 and it follows from this that the weakening of the color of the reagent solution when acted upon by the test solutions does not obey the Lambert Beer law.

Results are given in the table which characterize the accuracy of the results obtained on the determination of piperidine in pyridine.

It is clear from the table that it is possible to determine piperidine in pyridine at concentrations of 0.01% and higher with a fair degree of accuracy, by means of the method proposed.

Quantitative Determination of Piperidine in Pyridine by Means of Malachite Green

Content of piperidine in pyridine (%)	Piperidine taken, μg	Piperidine found, μg	Error in μg	Error in %
0.010	100	100	0	0.0
0.012	115	120	+5	-4.3
0.013	125	120	-5	4.0
0.014	135	135	0	0.0
0.015	150	150	0	0.0
0.017	175	175	0	0,0
0.020	200	207	+7	3.5
0.021	210	208	-2	0.9
0.023	225	225	0	0.0
0.025	250	250	0	0.0

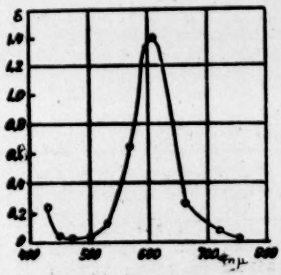

Fig. 1. Light absorption curve for a methanol-pyridine solution of malachite green.

EXPERIMENTAL

Reagent . The reagent used was a 0.1% solution of the pure dye, malachite green (for bacteriological purposes) in colorless, freshly distilled anhydrous pyridine. The dye dissolves on warming slightly; the solution thus obtained is colored a blue-green which quickly turns pale.

Reagent paper is prepared by soaking strips of filter paper in the reagent solution and drying at 60-70°. Where the reagent paper is to be used for detecting less than 0.1% piperidine, it is necessary to use a reagent solution of 0.05% malachite green (prepared by diluting the base solution of the dye twice) for soaking the strips. Both the reagent solution and paper are stable

Detection of Piperidine in Pyridine. A drop of the pyridine which is to be tested for piperidine is placed on the reagent paper by means of a capillary. If more than 0.1% of piperidine is present in the pyridine a stable white spot appears on the green background of the paper after a few seconds. For concentrations of piperidine less than 0.1%, complete decolorization is not observed, instead only a weakening of the color at the point where a drop of test solution was placed, occurs. This weakening of the color is compared with a spot obtained by the use of a drop of pyridine free from piperidine on the filter paper.

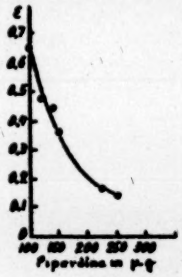

Fig. 2. Calibration curve for spectrophotometric determination of traces of piperidine in pyridine.

If the decolorization or weakening of the color is the result of the action of ammonia and not piperidine, the spot is unstable and its color soon becomes comparable with the general background.

The Quantitative Determination of Piperidine in Pyridine. To 1 ml of the pyridine to be tested contained in a test tube are added 0.5 ml of the 0.1% reagent solution of malachite green and 2.5 ml of pure methyl alcohol; the test tube is thoroughly shaken and placed on a water bath at 60-70° for 1-2 minutes.

The contents of the test tube after cooling are transferred to the cell of a photometer of the Pulfrich type with d = 5 mm and colorimetrically determined with a light filter S = 61; water is used as the condensing liquid. Calculations are made on the basis of a calibration curve prepared beforehand (Fig. 2).

We recommend that each investigator should prepare his own calibration curve for any given sample of malachite green. In addition it should be born in mind that high values for light absorption correspond to low concentrations of piperidine.

SUMMARY

1. A method is proposed for the qualitative (spot test) detection and quantitative (colorimetric) determination of traces of piperidine in pyridine.

2. The method is based on the formation of a complex compound between piperidine and malachite green.

3. By means of this method 1 μg of piperidine can be detected in pyridine for a ratio of piperidine to pyridine of 1:2000; it is possible to determine quantitatively amounts of 0.01% and over of piperidine in pyridine.

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A COLOR REACTION FOR DICHLOROETHANE

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1,2-Dichloroethane CH_2ClCH_2Cl (b.p. 83.5°) which is easily available finds considerable application as a volatile solvent for the extraction of fats and fatty substances, and in the preparation of various lakes, etc. [1].

Dichloroethane is toxic. The tolerance limit for it in the atmosphere of places of work is 0.05 mg/l [2]. In this connection, it is often necessary to detect the presence of dichloroethane either in the air, or as a component of mixed solvents. Existing methods for the detection and determination of dichloroethane are based on saponification or on combustion to HCl. The Cl ion is then determined nephelometrically with $AgNO_3$ [3,4,5]. It is obvious that all halogen containing compounds will thus be determined as dichloroethane.

We have been unable to find in the literature descriptions of any specific reaction for dichloroethane, which would enable it to be determined in the presence of other solvents. In the present article, a new color reaction which is specific for dichloroethane is described, and which is based on the formation of a red color on heating quinoline and dichloroethane.

Procedure

0.2-0.3 ml of quinoline which is not too dark or, better still, which is freshly redistilled (b.p. 238°) is placed in a test tube and one drop of dichloroethane, or the solvent suspected of containing dichloroethane added. The test tube is placed in a glycerine bath heated to 200° and left in it for 3-4 min. It is better to heat on an electric hot plate or on a gas burner. In the presence of a large amount of dichloroethane the quinoline on slow, prolonged, heating develops a brown or brownish-red color; on heating it quickly the color attained is a bluish-red color. For small amounts of dichloroethane the color of the quinoline becomes orange-yellow. In the absence of dichloroethane no color develops.

Dilution of the quinoline with indifferent solvents which boil below 200°, impairs the reaction, since the reaction has an optimum rate at 190-200°. The quinoline can be diluted two or three times with non-aqueous, colorless glycerine or naphthalene without significantly impairing the clarity of the reaction.

This reaction can be used for the detection of 5-10% of 1,2-dichloroethane in chloroform, xylene, carbon tetrachloride, chlorobenzene, 1,1-dichloroethane (ethylene chloride), and in a number of other solvents. If the content of dichloroethane is less than 5%, then it will be necessary to take several drops for the reaction. When colorless, freshly redistilled quinoline is used, the reaction can detect 0.1 mg of dichloroethane.

Dichloroethane vapor can be detected in the atmosphere by passing the air through a glass tube 10-12 cm long and 0.5 cm in diameter, containing glass wool and a plug of 2-3 cm length of dry, finely crushed silica gel, particle size 1 mm. For a considerable concentration of dichloroethane, more than 1 mg/l, it is sufficient to pass 1-2 liters of air. If the dichloroethane content is low, then a greater volume of air has to be passed through. The tube is moistened with a

few drops of quinoline and heated on an electric hot plate.[1] If the grains of silica gel redden after 2-3 minutes, the presence of dichloroethane in the air is confirmed. In the absence of dichloroethane the silica gel remains colorless.

Selectivity of the Reaction

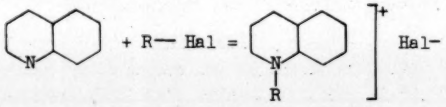
The following compounds do not give this reaction and no color is formed with quinoline. Hydrocarbons: benzene, toluene, xylene, gasoline, kerosene; halogenated hydrocarbons: chloroform, 1,1-dichloroethane (ethylene chloride, CH_3-CHCl_2), carbon tetrachloride, chlorobenzene, chloronaphthalene, polychloronaphthalenes (Halovaks); alcohols: methyl, ethyl, propyl, butyl, amyl alcohols; esters: amyl acetate, butyl acetate, ethyl acetate; ethers: diethyl, diisopropyl; acids: acetic, pyridine.

In addition to 1,2-dichloroethane the following give positive reactions with quinoline; ethyl bromide, 1,2-dibromoethane; ethyl iodide, ethyl chloride. Nevertheless we have never come across the use of the halogenated hydrocarbons just enumerated as solvents or as components of mixtures with dichloroethane either in practice or in the literature.

A Proposed Mechanism for the Reaction

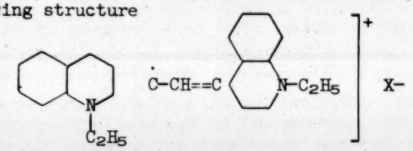
Investigations already carried out and still in progress enable us to propose the following mechanism for the reaction.

By the action of alkyl halides, quinoline, like any other tertiary amine, forms salts of a quaternary ammonium base;



the different alkyl halides react at different rates.

Quaternary quinoline salts on heating with alkaline solutions form intensely colored cyanine dyes, e.g. with ethyl iodide quinaldine, and quinoline forms a dye of the following structure



which gives solutions of an intense rose color. Dyes of this class have been studied extensively. There are a number of investigations and patents, describing methods of preparation and the properties of this class of dyes [6,7]. It has been pointed out also that analogous dyes are also formed from quinoline and alkylquinoline salts without participation of the alkyliodides of quinaldine and lepidine [8].

In this case the ease of conversion of quaternary quinoline salts into colored products also depends on the nature of the alkyl group. According to the nature of the alkyl radical which participates in the formation of colored compounds, the temperature and alkalinity of the medium must be varied.

The red products formed as a result of the color reaction for dichloroethane possess all the properties of cyanine dyes obtained from salts of methyl or ethyl quinoline. These products dissolve with the same red color in dilute

[1] It is important that the tube not rotate. When heat is applied to one side only, the heating proceeds nonuniformly, and there will always be found in the tube a region of nearly the optimum temperature.

acids and have colored cations, which are precipitated under the influence of large complex anions, such as HgI_4^{2-}, $Zn(SCN)^{2-}$, CdI_4^{2-}, etc. In a number of these cases typical "colored solid phase reactions" develop [9]. The behavior of the colored products formed during the reaction for dichloroethane on heating and to oxidizing or reducing agents and to other various reagents is also similar in all respects to the behavior of cyanine dyes to the same reagents, etc. It is permissible therefore to assume that cyanine dyes are formed during the reaction described.

The reason for the unexpectedly high selectivity of the reaction can only be explained by means of such a hypothesis. It is possible that 1,2-dichloroethane, in contrast to chloroform, 1,1-dichloroethane, chlorobenzene, carbon tetrachloride and others, gives the reaction because it either forms quaternary ammonium salts more easily than the others, or the salt is more easily converted into a dye, the alkalinity of the quinoline itself being high enough for the conversion.

The study of the reaction mechanism is being continued, together with work on the use of this new reaction for the quantitative determination of dichloroethane.

SUMMARY

When 0.2–0.3 ml of quinoline is heated in a test tube to boiling with a drop of 1,2-dichloroethane or a solvent which contains dichloroethane, an intense red color develops; 0.1 mg of dichloroethane can be detected by this reaction.

The reaction is highly selective; 1,1-dichloroethane, chloroform, carbon tetrachloride, various hydrocarbons, and many other substances enumerated above do not give this reaction.

The red color developed is apparently the result of the formation of cyanine dyes.

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REACTIONS FOR THE IDENTIFICATION OF DICHLOROETHANE

V. A. Nazarenko and N. V. Lapkina

It is sometimes necessary in practice to identify 1,2-dichloroethane. If a few drops of liquid are available for test then no special difficulty arises, since its characteristic smell, the determination of physical constants (specific gravity, b.p., etc.), together with some simple chemical tests (determination of organically bound Cl etc.), lead to a fairly complete identification of the product. It is considerably more difficult to solve the problem of identification when the internal organs (e.g. the stomach and its contents) are examined, and the distillate obtained for the determination of volatile poisons analyzed. In distillates of this kind, the dichloroethane, if present in small amounts, can be completely in solution in the water (the solubility of 1,2-dichloroethane at 20° is 0.869 g/100 ml). Similarily the vessel containing the liquid which has given rise to poisonous effects may contain such a small amount of the poison that the determination of physical constants is out of the question. The odor which resembles that of chloroform, in the absence of positive reactions for chloroform and in the presence of organically combined Cl can hardly be regarded as a reliable test for the identification of dichloroethane. The need therefore exists for a chemical reaction which can be used for the identification of dichloroethane, which is sensitive enough for application to aqueous solutions and which will enable dichloroethane to be distinguished at least from the most common chlorinated solvents, chloroform, carbon tetrachloride and trichloroethylene.

No characteristic chemical reaction is known for 1,2-dichloroethane in aqueous solution which can be used for distinguishing it from other chlorinated derivatives of methane and ethane. Nevertheless it can be converted into other compounds - ethylene glycol, acetylene and ethylendiamine, which can easily be identified by well known chemical reactions.

In the present article the possibility of detecting dichloroethane by its conversion into other compounds is considered.

1. Detection of Dichloroethane by the Formation of Ethylene Glycol

1,2-Dichloroethane is slowly hydrolyzed by water, with the formation of ethylene glycol. The reaction velocity increases considerably in the presence of Na_2CO_3, particularly on heating under pressure. Ethylene glycol in turn can be detected by the formation of formaldehyde when reacted with acid periodate solution. Finally formaldehyde is detected by Schiff's reagent. This reaction occurs not only with pure dichloroethane but also its aqueous solution.

Procedure. 0.5 ml of the aqueous test solution is introduced by means of a pipette into a 1 ml glass ampoule; this is followed by the addition of 0.5 ml of a 10% solution of Na_2CO_3. The ampoule is sealed and placed for 1 hour on a steam bath. After cooling, the ampoule is opened and the liquid transferred by means of a pipette into a small test tube. 6-7 drops of H_2SO_4 (1:8) are added until the solution is acid and then 2 drops of a 5% solution of K or Na periodate 1 N H_2SO_4 added and left for 5 minutes. Finally a saturated solution of H_2SO_3 is added until the iodine which initially separates out disappears, 2 drops of Schiff's reagent added. The appearance of a rose color indicates the presence of dichloroethane. For small amounts of dichloroethane the color only appears after

10-25 minutes. A color which develops only after 35-40 minutes should be ignored.

By this method it is possible to detect 0.4 mg of dichloroethane in aqueous solution at a dilution of 1:1200.

2. Detection of Dichloroethane by the Formation of Acetylene

Vinyl chloride is formed by the action of strong caustic on 1,2-dichloroethane. If the reaction is carried out in a closed vessel under pressure, then a further conversion of the vinyl chloride to acetylene takes place. The acetylene formed can then be detected by reacting it with an ammoniacal solution of Cu [1]. The reaction is given by aqueous solutions of dichloroethane.

Procedure. 0.5 ml of the aqueous solution of dichloroethane is introduced into a 1 ml ampoule and 0.5 ml of 30% NaOH added by means of a fine capillary tube, so that as far as possible the liquids do not mix. The ampoule is sealed, the liquids mixed by shaking, and then heated on a steam bath for 30 minutes. When it is cold again, the ampoule is opened and the liquid transferred into a test tube by means of a pipette. A 30% acetic acid solution is added dropwise to the contents of the test tube until the solution is acid to litmus, when 2 drops of an ammoniacal solution of Cu are added. If 1,2-dichloroethane is present, a rose or cherry red color develops and gradually a precipitate of the same color settles out. 0.25 mg of 1,2-dichloroethane at a dilution of 1:2000 can be detected in this way.

The ammoniacal solution of Cu is prepared by dissolving 1 g $CuNO_3$ and 4 g of hydroxylamine hydrochloride in a small amount of water, 5 ml of 20% ammonia is then added to the solution obtained and the whole shaken until the solution is colorless when it is made up to 50 ml with water.

3. Detection of Dichloroethane by the Formation of Ethylenediamine

When 1,2-dichloroethane is heated with a concentrated solution of ammonia under pressure, ethylenediamine is formed. The ethylenediamine can be detected by a microcrystalloscopic reaction with potassium bismuth iodide with which it forms characteristic rod shaped crystals of a bismuth iodide complex. Since polyamines are also formed during the reaction between 1,2-dichloroethane and ammonia, other crystals can be seen under the microscope besides the rod shaped ones, viz., rectangular and square shaped crystals. This reaction is only applicable to liquid dichloroethane, it cannot be used for aqueous solutions.

Procedure. A drop of dichloroethane (0.001-0.005 ml) is introduced into a 1 ml ampoule and 0.5 ml of a 25% ammonia solution added, after which the ampoule is sealed, and heated on a steam bath for 1 hour. When cool the contents are transferred into a small beaker and evaporated to dryness. The residue is dissolved in 1-2 drops of water. To a drop of the solution a drop of potassium bismuth iodide is added. At first an amorphous suspension is formed which gradually crystallizes out as blood red crystals in the form of short rods, squares, and rectangles, and aggregates of these respective forms.

4. The Specificity of the Reactions for 1,2-Dichloroethane

The three reactions described above were tested on different halogenated derivatives of methane and ethane. Results are given in the table for tests carried out with both aqueous solutions and with small amounts (3-10 mg) of liquid or crystalline halogenated derivatives. From the table it may be observed that the formation of ethylenediamine and ethyleneglycol for a series of halogen derivatives of methane and ethane is specific for 1,2-dichloroethane. Allyl bromide gives a very definite reaction with the Schiff's base, probably as the

result of the formation of allyl alcohol during saponification with Na_2CO_3, the allyl alcohol on oxidation with periodate yielding formaldehyde. It should be noted that the samples of 1,1-dichloroethane and 1,1,1-trichloroethane which we tested also gave a weak positive reaction for ethyleneglycol, but this can probably be explained by the presence of small amounts of 1,2-dichloroethane in them, since the intensity differed for different samples and diminished in proportion to the extent of purification of these substances by fractional distillation.

The formation of acetylene is less specific than the other, since 1,1-dichloroethane, 1,1,2-trichloroethane behave similarily to 1,2-dichloroethane. 1,1,1,2-Tetrachloro- and tetrabromoethane, tribromoethylene and acetylene chloride under the same conditions give a profuse yellow turbidity, which on long standing for many hours changes into a red, flocculent precipitate characteristic of copper acetylide.

No.	Compound	Reaction for Formation of		
		Ethyleneglycol	Acetylene	Ethylene-diamine
1	Chloroform	–	–	–
2	Carbon tetrachloride	–	–	–
3	Monochloroethane	–	–	–
4	1,1-dichloroethane	–	+	–
5	1,2-dichloroethane	+	+	+
6	1,2-dibromoethane	+	+	+
7	1,1,1-trichloroethane	–	–	–
8	1,1,2-trichloroethane	–	+	–
9	1,1,1,2-tetrachloroethane	–	–	–
10	1,1,2,2-tetrachloroethane	–	Yellow turbidity	–
11	1,1,2,2-tetrabromoethane	–	Ditto	–
12	Pentabromoethane	–	–	–
13	Hexachloroethane	–	–	–
14	Tribromoethylene	–	Yellow turbidity	–
15	Acetylenedichloride	–	Ditto	–
16	Chloral	–	–	–
17	Bromallyl	+	–	–

5. How to Distinguish Between 1,2-Dichloroethane and 1,2-Dibromoethane

1,2-Dibromoethane, like 1,2-dichloroethane, gives all the three reactions described above: in order to distinguish between them the reactions for chloride and bromide are used. A drop of the liquid halogen derivative, or 0.5 ml of an aqueous solution of it, is heated with 0.5 ml of 25% ammonia in a sealed ampoule on a steam bath for 1 hour as described above for the formation of ethylenediamine. The liquid obtained is then evaporated to dryness in a small beaker and the residue dissolved in two drops of water. One drop is used for a chloride reaction with diphenylcarbazide after separation of the chromyl chloride, and the other drop for a fluorescein test for bromide.

SUMMARY

1,2-Dichloroethane can be identified by means of three reactions: 1) by conversion into ethyleneglycol by heating with Na_2CO_3 under pressure. Ethylene glycol is subsequently identified by the formation of formaldehyde by oxidation of the glycol with periodate.

2) Conversion into acetylene on heating with NaOH under pressure, the acetylene being identified by the formation of Cu acetylide. 3) Conversion into ethylendiamine on heating with ammonia; the ethylenediamine is detected by a reaction with potassium bismuth iodide.

The first two reactions can be used for the detection of 1,2-dichloroethane in aqueous solutions. The sensitivity of the first reaction is 0.4 mg (1:1200) and of the second 0.25 mg (1:2000).

The formation of ethylene glycol and ethylendiamine is specific for 1,2-dichloroethane from a series of ethane and methane halogen derivatives tested.

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RAPID METHODS OF MICROELEMENTARY ANALYSIS

V. A RAPID METHOD FOR THE DETERMINATION OF CARBON AND HYDROGEN

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In previous papers we have described a new, rapid method for the micro and semi-micro determination of carbon and hydrogen [1], in which we showed that it is possible to carry out a quantitative combustion of a substance in a large excess of oxygen without the use of oxidizing agents and catalysts, but under such conditions that a preliminary pyrogenetic decomposition of the substance is ensured with almost complete exclusion of oxygen. If this method is used without the use of preliminary pyrolysis, a quantitative oxidation of the organic compound is impossible.

From these experiments it became clear to us that the method of decomposition of an organic compound can play an essential role in the determination of carbon and hydrogen.

Combustion of an organic compound in an empty tube, in which only gaseous oxygen is used, enables us to pose the question as to the part played by the method of decomposition in influencing the path taken by the oxidation, i.e. to examine more closely the process of decomposition during an analysis. To solve such a problem experimentally by means of tubes containing "universal" packings is of course impossible.

In fact, the attention of analytical chemists concerned with micro analytical determinations of the elementary composition of organic compounds, has been concentrated on the quantitative oxidation of substances by combustion mainly at the expense of solid oxidizing agents and catalysts in the presence of oxygen or air, and the question of the part played by the method of decomposition used has never been touched upon.

E. G. Weygand [2], in considering the micro analytical determination of carbon and hydrogen, came to a completely erroneous conclusion.

In 1948 Weygand wrote that the possibility of combustion analysis of organic compounds in the presence of catalysts "looked very attractive". But the author encountered difficulties during catalytic combustion of compounds and therefore concluded that "oxidation by the means of chemical methods is always more reliable" by which he meant the use of an "universal" filler for the combustion tube, as proposed by Pregl. This consists of CuO, $PbCrO_4$, PbO_2, Ag, and asbestos. Weygand however warned that only the Ag can be regarded as being above suspicion with regard to purity, while asbestos, CuO, and $PbCrO_4$ possess considerable disadvantages. Completely reliable CuO and $PbCrO_4$ are not available. In spite of this, Weygand prefers to carry out combustions according to the Liebig-Pregl method and describes it in detail in his book. In the meantime as we have shown in earlier work [3-5] the catalytic method of combustion is more reliable than the Liebig-Pregl method.

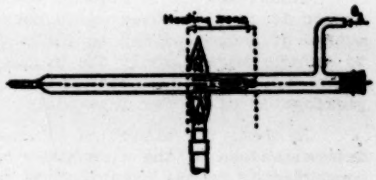
The most reliable and simple method seems to be the rapid combustion method in an empty tube. As regards the method of decomposition we are convinced that it is of considerable significance for any of the methods in existence for the determination of carbon and hydrogen. This can only be proved experimentally by combustion in an empty tube.

Observations [1] on the path taken by the decomposition of a compound when using rapid pyrolysis gave us a basis for proposing that a large part of the volatile products of thermal decomposition is oxidized almost completely on coming out of the section of the tube in the short, red hot zone of the combustion tube heated by a movable burner.

Further observations on the part played by the method of decomposition of a substance under the conditions which we worked out for the rapid method of determination of carbon and hydrogen led us to the most interesting results.

Experiments were carried out on the determination of carbon and hydrogen in certain organic compounds by means of the rapid method and the apparatus described previously [1]. The only difference was that combustion of the organic compound was effected by means of only one gas burner. No electric heater was used, and the burner used was not moved outside the zone limits marked by arrows in the diagram. The heating zone during each stage of the combustion was never more than 2-3 cm in these experiments, i.e. the width of the gas burner flame. The oxygen throughput was 35-40 ml/minute. The duration of combustion and sweeping out did not exceed 10-12 minutes. The oxygen rate indicated above was sufficient to clear away the water condensed on the cold parts of the combustion tube quantitatively.

The results obtained exceeded all expectations. From the examples adduced in Table 1 (combustion with pyrolysis) it can be seen that 95% and sometimes even 100% of the carbon contained in the test material was oxidized to CO_2, while the hydrogen in all cases was quantitatively converted into H_2O. On the other hand on carrying out the combustion in a boat under the other conditions described above, even the hydrogen was not oxidized completely (Table 2).



Scheme for Combustion

Thus it can be assumed that when the method of decomposition in a boat is used, oxidation of the material proceeds basically in that zone of the combustion tube which is heated by a long burner or an oven.

The fact that hydrogen in all the cases of combustion with pyrolysis is quantitatively converted into H_2O indicates that hydrogen is a basic product of the decomposition of a substance during pyrolysis of a compound.

The insignificant amount of carbon which is not completely oxidized to CO_2 when only one burner is used for combustion was found by us both qualitatively and quantitatively to have been converted into CO.

The results for the determination of carbon and hydrogen by means of combustion with one burner is of special interest for substance 3, Table 1, since it consists of a condensed ring with an angular methyl group. Even in such a difficult case as this where it would be expected that methane would be produced as the product of pyrolysis, we obtained theoretical values for hydrogen

and only 3.7% (absolute) less carbon than theoretical.

TABLE 1

Combustion with Pyrolysis

Compound	Wt. taken, mg	Amt. Found %		Amt. Computed %		ΔC in % absol.	ΔH in % absol.	ΔC in % relative	ΔH in % relative
		C	H	C	H				
Naphthalene ($C_{10}H_8$)	5.080	92.05	6.27	93.70	6.30	-1.65	-0.03	-1.77	-0.48
	4.890	92.33	6.17	-	-	-1.37	-0.13	-0.47	-2.17
	4.345	93.67	6.23	-	-	-0.03	-0.07	-0.04	+1.02
Laevulose ($C_6H_{12}O_6$)	5.180	38.11	6.75	39.98	6.67	-1.87	-0.08	-4.68	+1.19
	4.500	35.93	6.77	-	-	-4.05	-0.10	-10.14	+11.49
9,10-(2,5-Dimethyl-2-cyclopentene-3-ol-4-one), 1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene ($C_9H_{26}O_2$)	6.580	75.96	9.07	79.67	9.15	-3.7	-0.08	- 4.66	-0.88
Methylhexahydrophthalic acid ($C_9H_{14}O_4$)	4.922	58.10	7.71	58.06	7.52	+0.04	+0.19	+0.06	+2.52
	4.022	57.76	7.70	-	-	-0.50	-0.18	-0.87	+2.39
Picric acid[1] ($C_6H_3O_7N_3$)	4.950	31.12	1.29	31.44	1.32	-0.32	-0.03	-1.02	-2.68
	4.520	30.44	1.39	-	-	-1.00	+0.07	-3.19	+5.30

TABLE 2

Combustion in a Boat

Compound	Wt. taken, mg	Amt. Found %		Amt. Computed %		ΔC in % absol.	ΔH in % absol.	ΔC in % relative	ΔH in % relative
		C	H	C	H				
Naphthalene ($C_{10}H_8$)	4.215	5.30	0.67	93.70	6.30	-88.40	-6.63	-94.35	-89.37
Methylhexahydrophthalic acid ($C_9H_{14}O_4$)	4.330	7.39	2.62	58.06	7.52	-50.67	-4.90	-87.28	-65.16

It is of interest to note that for the combustion of similar materials, six layers of filling for the combustion tube consisting of CuO and platinized asbestos are proposed in a contemporary American textbook: Niederl and Niederl [7]. If combustion of a compound were carried out with pyrolysis, then doubtless it should be possible to achieve quantitative oxidation of similar substances in the presence of only (a) a catalyst or (b) "a universal" Pregl filler even under the conditions employed in the "classical" methods of analysis.

1) Oxides of nitrogen were trapped by solid absorbents prepared according to Klimov's method [6].

By numerous experiments on combustion with one burner it was established that during the pyrolytic decomposition of an organic compound, almost complete oxidation with the use of gaseous oxygen only is achieved during the time the products of decomposition are in the very short zone heated by the gas burner and during the very short time (2-secs) when the substance is in this zone. (For a rate of 35-40 ml/minute of oxygen, a diameter of combustion tube of 9 mm and length of heated zone 20-30 mm, the contact time with oxygen is 2-3 sec.)

All the hydrogen in the molecule is oxidized to H_2O under these conditions. 95-100% carbon is oxidized to CO_2 and only up to $\sim$5% of the carbon remaining oxidized to CO.

It is obvious that subsequent oxidation in the zone heated electrically proceeds far easier than has been assumed up to the present.

It should be observed that this type of investigation on the decomposition of compounds has not been described in the literature. Apart from its theoretical interest, this investigation enables practical conclusions to be drawn, in particular the following: for a rapid determination of carbon and hydrogen a long heating zone is unnecessary, i.e., the length of the heaters and the length of the combustion tube. Thus a tube length of 33-38 cm should be sufficient instead of 62 cm and a heater length of 8-10 cm instead of 25-30 cm.

In Table 3 results are given for determinations of carbon and hydrogen in compounds of different composition and structure. Combustion of these compounds was carried out in a 36 cm tube with an electrical heater of 10 cm length at a temperature of 950°.

For the analysis of liquids of low boiling point (Table 3) we used the technique for combustion of volatile substances, described previously [1]. The combustion method used for pentane and cyclopentane was modified somewhat. In these cases aliquots were taken in a sealed capillary which was then opened in the tube. The capillary as usual was placed in an ampoule with a sealed end. That part of the tube where the widened part of the capillary is located was then cooled with ice, while its sealed end was simultaneously heated.

After the capillary had been opened, the opened end was cooled and at the same time the burner was placed at the opened end of the ampoule in which the capillary was located.

In this way we managed to get satisfactory results for pentane and cyclopentane boiling in the range 34-45°.

SUMMARY

1. It has been shown that the method used for the decomposition of a compound during combustion has an effect on the ease with which it is oxidized. Oxidation of a substance to CO_2 and H_2O (95-100%) by a pyrolytic method of decomposition is achieved in the short zone heated by a gas burner, and in the very short time, 2-3 sec., during which the material is in this zone.

2. When the rapid method for the determination of carbon and hydrogen in a large excess of oxygen is used there is no need for a large zone, i.e. for long heaters and combustion tubes. Even for analysis of volatile materials, tubes of 33-38 cm and a heating zone of 10 cm are adequate.

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TABLE 3

Compound used and empirical formula	Carbon, %			Hydrogen, %		
	Found	Computed	Diff.	Found	Computed	Diff.
10,14,17-Trimethyl-Δ^{8}-dodecahydrocyclopentanophenanthrene-3,15-dione ($C_{20}H_{28}O_2$)	79.82	79.96	−0.14	9.30	9.39	−0.09
	79.71	–	−0.25	9.28	–	−0.11
The diacetate of 3,5,7,9-tetramethylbicyclopentane-dihydroxy-$\Delta^{6,11}$-diene-1,2-dione ($C_{18}H_{22}O_7$)	61.85	61.70	+0.15	6.26	6.33	−0.07
	61.63	–	−0.07	6.23	–	−0.10
Semicarbazone 9-methyl-6-methoxy-Δ^{6}-octalone-1 ($C_{13}H_{21}O_2N_3$)	62.10	62.10	0.00	8.51	8.40	+0.11
	62.38	–	+0.18	8.22	–	−0.18
10,14,17-Trimethyl-Δ^{8}-dodecahydrocyclopentanophenanthrene-15-one ($C_{20}H_{30}O$)	83.93	83.85	+0.08	10.78	10.80	−0.02
	83.75	–	−0.10	10.68	–	−0.12
9-Methyl-1-ethinyl-1-decalol-6-one ($C_{13}H_{18}O_2$)	75.91	75.70	+0.21	8.83	8.80	+0.03
	75.88	–	+0.18	8.92	–	+0.12
2,3-Dimethylbicyclo-(2,2,2) octane ($C_{10}H_{18}$)	87.05	86.88	+0.17	13.28	13.12	+0.16
	86.98	–	+0.10	13.08	–	−0.04
17-Methyl-$\Delta^{2,16}$-1,4,8-triketotetradecahydrochrysene ($C_{18}H_{22}O_3$)	76.20	76.48	−0.28	7.53	7.43	+0.10
	76.49	–	+0.01	7.60	–	+0.17
Tri-(α-isopropoxy)-ethyl ether of triethanolamine ($C_{21}H_{45}O_6N$)	61.73	61.92	−0.19	11.17	11.06	+0.11
	61.88	–	−0.04	11.15	–	+0.09
Di-(α-isopropoxy)-ethyl ether of diethanolamine ($C_{14}H_{31}O_4N$)	60.47	60.61	−0.14	11.26	11.26	0.00
	60.41	–	−0.20	11.37	–	+0.11
1-Methyl-3-ethylcyclobutane (C_7H_{14})	85.61	85.63	−0.02	14.39	14.37	+0.02
trans-form B.p. 87.9-88.1°	85.64	–	+0.01	14.40	–	+0.03
Cis form B.p. 91-91.1°	85.56	85.63	−0.07	14.27	14.37	−0.10
	85.53	–	−0.10	14.43	–	+0.06
2-Methylpentane (C_6H_{14}) B.p. 58.5-59°	83.78	83.63	+0.15	16.33	16.37	−0.04
	83.80	–	+0.17	16.44	–	+0.07
Pentane (C_5H_{12}) B.p. 35-36°	83.12	83.24	−0.12	16.68	16.76	−0.08
	83.61	–	+0.37	16.95	–	+0.29
Cyclopentane (C_5H_{10}) B.p. 40-45°	85.33	85.63	−0.30	14.65	14.37	+0.28
	85.20	–	−0.43	14.72	–	+0.35
1,3-Dimethylcyclobutane (C_6H_{12}) Trans form B.p. 57.4-57.6°	85.45	85.63	−0.18	14.53	14.37	+0.16
	85.42	–	−0.21	14.39	–	+0.02
3-Methylpentane (C_6H_{14}) B.p. 60-64°	83.88	83.63	+0.25	16.36	16.37	−0.01
	83.53	–	−0.10	16.35	–	−0.02

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RAPID METHODS OF MICROELEMENTARY ANALYSIS

VI. THE MECHANISM OF THE FORMATION OF SILVER SULFATE DURING THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND SULFUR IN ORGANIC COMPOUNDS

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In 1948 we demonstrated the possibility of using the principle of rapid combustion for the determination of carbon and hydrogen in an empty tube for the simultaneous determination of carbon, hydrogen and sulfur on one aliquot of 4-6 mg [1].

The absorption of all the products of combustion within the limits of the tube enables one to determine any sulfur present in a compound simultaneously with carbon and hydrogen, the sulfur being trapped by metallic silver in a specially constructed apparatus. It is obvious that a quantitative determination of sulfur by the method indicated anticipates the conversion of all the "organic' sulfur by the silver to ions containing sulfur. The trapping of the oxides of sulfur by silver was first used by Dennstedt [2] in the catalytic method he developed for the determination of carbon and hydrogen.

Almost 40 years afterwards, the possibility of using this reaction between metallic silver and sulfur oxides for the quantitative determination of sulfur in organic compounds [3] was beginning to be reconsidered. Later some authors used silver for developing a method for the determination of sulfur by the catalytic combustion of a compound in a stream of oxygen. According to this method, on completion of combustion the silver is extracted from the combustion tube and the silver salt formed dissolved. Further the sulfur was determined electrolytically by weighing the silver deposited on the cathode [4] or the percentage sulfur was calculated from the loss in weight of the silver mesh after dissolving out the silver salts.

The mechanism of the reaction through which the quantitative formation of Ag_2SO_4, by the interaction of metallic silver with sulfur oxides, proceeds was up to this time unknown.

Dennstedt [2] considered that in the catalytic decomposition of organic compounds containing sulfur, the greater part reacts with silver to form Ag_2SO_4. However, this assumption is of special significance since it is only justified in those cases where the test compound contains sufficient hydrogen. Ag_2SO_4 can be obtained quantitatively even during the analysis of elementary sulfur in a stream of dry oxygen [6].

Other authors [3] in their study of the mechanism of this reaction consider it most probable that SO_3 reacts directly with heated silver, forming Ag_2SO_3 which is immediately oxidized to Ag_2SO_4 in the presence of oxygen.

This hypothesis also does not appear to be substantiated since at those temperatures at which sulfur is trapped by silver, Ag_2SO_3 is not oxidized to the sulfate, but on the other hand actually decomposes, giving SO_2 and thus losing 30% of its sulfur.

Thus, all the existing hypotheses on the mechanism of the interaction between sulfur oxides and silver seem to us to be improbable, the more so since they are derived from the assumption that Ag_2SO_4 is formed from SO_3 and silver. The formation of Ag_2SO_4 by the interaction of silver with SO_2 in general has not been mentioned. Meanwhile, during the combustion of organic compounds containing sulfur at atmospheric pressure in a stream of oxygen, the predominant formation of SO_2 or SO_3 depends on the temperature, the concentration of excess oxygen, and the presence or absence of catalysts.

According to Knietsch's results [7] on the chemical equilibrium between SO_2 and SO_3 in the presence of oxygen and platinum, 400° is the optimum temperature for 100% formation of SO_3 according to the equilibrium:

$$2SO_2 + O_2 \rightleftarrows 2SO_3.$$

None of these authors mentioned above [2-6] worked at temperatures lower than 600°, at which temperature only 80% SO_3 is formed. We worked at even higher temperatures so that the conditions in our method are not optimum for the formation of SO_3. At 950°, even in the presence of platinum catalysts, the equilibrium of the above reaction is strongly shifted to the left, i.e. towards the formation of SO_2. Consequently, under our conditions, the sulfur is most likely to be oxidized to SO_2 which, as our experimental results show, reacts afterwards with silver with quantitative formation of Ag_2SO_4.

TABLE 1

Combustion of the $C_8H_{11}O_2$ Mercaptan. Computed % S – 18.19

Wt. taken	Amount of 0.02 NI_2 used in ml	S as SO_2 %	Experimental Conditions
4.700	2.62	97.85	Combustion with one burner
7.130	3.80	93.43	Combustion with an electric furnace 10 cm long at 950°C.
6.902	1.55	38.21	Same conditions but with Pt contacts.

Such a treatment of the question disproves the hypothesis discussed above re the formation of Ag_2SO_4, only by the interaction of silver with SO_3. We have shown however precisely which oxides of sulfur react with silver in the apparatus.

In order to solve the question we carried out a series of experiments with a mercaptan (1-methoxy-5-methylhexane-5-thiol-3-one) on the assumption that under the conditions of our method, its combustion should proceed with predominant formation of SO_2.

The products of combustion in these experiments were trapped with 2 ml of 0.02 N alkali, with subsequent iodometric determination of SO_2 [8].

The results given in Table 1, show that on combustion of this mercaptan with only one burner [9] and with the use of an electric heater, 98% of all the sulfur in the molecule was obtained as SO_2, while at a temperature of 950° with a heating zone of 10 cm, in the absence of platinum contacts, 93.4% of the sulfur was found in the form of SO_2. In the presence of platinum contacts and under similar experimental conditions 38% of all the sulfur was as SO_2.

We thus established that combustion of this mercaptan with one burner leads to almost quantitative formation of SO_2 from the sulfur.

Further combustions of the same mercaptan were carried out with the inclusion of a furnace, but in which the SO_2 was trapped at 700° by silver, and the H_2O and CO_2 by the usual methods. Equally satisfactory results were obtained for carbon, hydrogen and sulfur (Table 2).

TABLE 2

Combustion of a Mercaptan: Computed %: C-54.50; H-9.16; S-18.19

Wt. in mg	Wt. CO_2 in mg	Wt. H_2O in mg	Wt. SO_4 in mg	Found %			Diff., Absol. %		
				C	H	S	C	H	S
4.133	8.234	3.462	2.218	54.37	9.37	17.91	-0.13	+0.22	-0.28
4.695	9.333	3.880	2.512	54.25	9.25	17.86	-0.25	+0.10	-0.33

The following experimentally established facts can therefore be listed:

1) The presence of H_2O is not essential to ensure that heated silver will react with sulfur oxides to form Ag_2SO_4; Ag_2SO_4 is quantitatively formed even during the combustion of elementary sulfur in a dry stream of oxygen.

2) Ag_2SO_3 is not oxidized by a stream of oxygen to Ag_2SO_4 in the absence of silver, on the other hand, at a high temperature (650°) decomposition of Ag_2SO_3 with formation of SO_3 (ca. 30%) occurs.

3) Silver heated to 650-800° reacts with a mixture of SO_2 and SO_3 and hydrogen passing over it with the quantitative formation of Ag_2SO_4.

4) The formation of Ag_2SO_4 proceeds independently of whether the silver comes in contact with SO_2, or SO_3 or a mixture of the two.

These facts disprove the opinion that quantitative formation of Ag_2SO_4 can be the result only of a reaction between silver and SO_3 in a stream of oxygen.

On the basis of these experimental results we think that the following hypothesis may be advanced for the mechanism of the absorption of sulfur oxides by silver; metallic silver during combustion completely converts any sulfur oxides coming in contact with it into Ag_2SO_4, and thus seems to be a unique catalyst participating in the formation of the end products of the reaction.

SUMMARY

1. It has been established that during the combustion of compounds containing carbon, hydrogen and sulfur under our experimental conditions, the sulfur is evolved as a mixture of SO_2 and SO_3, the ratio of which is determined by the equilibrium

$$2SO_3 \rightleftarrows 2SO_2 + O_2,$$

which depends on the temperature, the oxygen content of the mixture, and other experimental factors.

2. It has been established that heated silver reacts with SO_2 and SO_3 under the conditions of the given method with quantitative formation of Ag_2SO_4. The formation of Ag_2SO_4 proceeds independently of whether the silver comes into contact with SO_2 or SO_3 or a mixture of the two.

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RAPID METHODS OF MICROELEMENTARY ANALYSIS

VII. A NEW METHOD FOR THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND SULFUR IN ORGANIC COMPOUNDS CONTAINING C, H, O, N AND S.

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We established [1,2] that at a temperature of 750° metallic silver quantitatively traps sulfur oxides. The increase in weight of the tube containing the silver was shown to correspond exactly to the weight of SO_4 and consequently the factor for calculating S is $S/SO_4 = 0.3338$.

The accuracy of the results for sulfur determined simultaneously with carbon and hydrogen by the method we developed previously lies within the limits (0.5-1.5%). As we showed later the reason for the low results for sulfur is probably the condensation of an insignificant amount of sulfuric acid in that part of the combustion nozzle where a rubber connection was used. On changing over to an apparatus for trapping sulfur which was connected through a ground glass joint to the combustion tube, we got completely satisfactory results.

Temperature of the Silver

There are quite a number of contradictory results in the literature regarding the temperature to which the silver should be heated for quantitative trapping of sulfur oxides. Some consider that 665° is the optimum temperature. Huffmann [3] considers 350° to be the optimum temperature, but at the same time states that at 550°, silver becomes most active. Others use the silver for trapping sulfur oxides at 800° [4].

Experiments which we carried out on the determination of sulfur in toluenesulfamide, in which the sulfur oxides were trapped with silver at temperatures ranging from 420-700°, showed that particularly low values were obtained for sulfur content in the temperature range 420-600°. This lowering of the true value of sulfur decreased on increasing the temperature to which the silver was heated. The results obtained were as follows:

Temperature of silver in °C	420	500	600	700
Sulfur found %	6.0	13.0	17.54	18.73
Sulfur computed %	-	18.73		

Further observations showed that the range 650-700° may be regarded as the optimum temperature range for the quantitative formation of Ag_2SO_4 for conditions of rapid combustion in a large excess of oxygen.

We observed quantitative formation of Ag_2SO_4 at 800° also. The necessity of using such a high temperature may become apparent in the determination of C, H and S without the use of an electric furnace for the combustion tube. That it is possible to adopt such a procedure for the simultaneous determination of C, H and S in which the only oxidizing zone for the decomposition products of the test material is heated metallic silver, was demonstrated by experimental results

published previously [1]. It should be observed nevertheless that at such a high temperature the tube containing the silver becomes strongly corroded and often gets out of order. In the present work therefore we maintained an oxidizing zone in the combustion tube by means of an electric furnace, and worked at a silver temperature of not more than 700°.

TABLE 1

Determination of Sulfur in Toluenesulfamide at Different Temperatures for the Silver. Computed: 18.73%

Ag. Temp. in °C	Wt. taken in mg	Wt. SO_4 in mg	S Found in % abs.	Experimental Conditions
420	4.730	0.465	3.28	Combustion in a stream of O_2
420	3.640	0.635	5.82	at a rate of 35-40 ml^2/min,
420	8.860	2.110	11.96	length of heating zone of
520	6.070	1.695	9.32	combustion tube 10 cm at a
540	4.905	2.430	16.54	temperature of 950°C.
600	4.102	2.155	17.54	
620	4.580	2.550	18.58	
640	5.450	3.082	18.88	
700	3.636	2.060	18.91	
700	4.522	2.538	18.73	
740	5.359	2.995	18.65	

The Temperature of the Oxidizing Zone With and Without Platinum Catalysts

Since we were not interested in introducing radical changes into the methods of determining carbon and hydrogen which we developed previously, in which quantitative oxidation of compounds containing C, H, O and N proceeds in the absence of platinum contacts exclusively at the expense of a large excess of oxygen heated to 950°, then it was of interest to carry out simultaneous determinations of carbon, hydrogen and sulfur under the same conditions.

Compounds in which sulfur was in a reduced form – sulfides, mercaptans – were of special interest. It is natural that the oxidation of bivalent sulfur under our experimental conditions should be more difficult than that of sulfur in an oxidized form. Experiments with ditolyldisulfide, thianthrene, mercaptan (1-methoxy-5-methylhexane-5-thiol-3-one) and dithiane (Table 2) showed equally good results for carbon, hydrogen and sulfur both with and without platinum catalysts.

We thus established that at a temperature for the oxidizing zone of 950°, analyses could be carried out without platinum contacts. A large number of simultaneous determinations of carbon, hydrogen and sulfur in different organic compounds was made, the results of which are given in Table 3.

It is clear from these examples that equally accurate results can be obtained for sulfides, disulfides, mercaptans, sulfones and other compounds independently of their sulfur content.

Apparatus

As pointed out above, determination of sulfur by the method worked out previously could be carried out with an accuracy of from 0.5–1.5%, the low results being the consequence of the condensation of insignificant amounts of sulfuric acid at the junction of the combustion tube where a rubber connection was used [2].

TABLE 2

Simultaneous Determination of C, H and S with and without Platinum Contacts

Designation of Compound and Empirical Formula	Pt. contacts used or not	Wt. in mg	Wt. in mg			Found in %			Diff. in %		
			CO_2	H_2O	SO_4	C	H	S	C	H	S
Thianthrene ($C_{12}H_8S_2$)	No	5.170	12.620	1.760	4.610	66.62	3.81	29.76	0.00	+0.08	+0.11
Computed %:	No	6.105	14.875	2.030	5.425	66.49	3.72	29.66	-0.13	-0.01	-0.01
C-66.62;	Yes	4.940	12.110	1.700	4.390	66.90	3.35	29.66	+0.28	+0.12	+0.01
H-3.73;											
S-29.65.											
Mercaptan 1-methoxy-5-methylhexane-5-thiol-3-one ($C_8H_{16}O_2S$)	Yes	4.900	9.800	3.990	2.652	54.58	9.11	18.07	+0.08	-0.05	-0.12
	No	4.366	8.690	3.580	2.370	54.32	9.18	18.12	-0.18	+0.02	-0.07
Computed %:											
C-54.50;											
H-9.16;											
S-18.19.											
2,5-Dimethyl-tetrahydro-1-thiopyryl-idene-4-acetic acid ($C_2H_{14}O_2S$)	Yes	4.348	9.208	3.028	2.205	57.80	7.79	16.93	-0.23	+0.21	-0.25
	No	4.957	10.550	3.345	2.530	58.08	7.55	17.04	+0.05	-0.03	-0.14
Calculated %											
C 58.03;											
H 7.58;											
S 17.18.											
Dithiane ($C_4H_8S_2$)	Yes	4.452	6.545	2.605	7.122	40.12	6.55	53.40	+0.06	-0.15	+0.26
Computed %:	Yes	5.290	7.788	3.253	8.410	40.18	6.88	53.06	-0.18	+0.18	-0.28
C-39.97;	No	5.460	8.030	3.320	8.720	40.13	6.80	53.31	-0.03	+0.10	-0.03
H-6.70;	No	4.605	6.790	2.800	7.385	40.24	6.80	53.53	+0.19	+0.10	+0.15
S-53.34.											
Ditolyldi-sulfide	Yes	4.860	12.135	2.585	3.780	68.14	5.95	25.96	-0.10	+0.23	-0.07
	No	5.470	13.645	2.775	4.270	68.07	5.68	26.05	-0.17	+0.06	+0.02
$C_{14}H_{14}S_2$											
Computed %:											
C-68.24;											
H-5.73;											
S-26.03											

It was essential therefore to construct a quartz combustion tube which could be connected with the apparatus containing silver by means of a ground glass joint.

The new model of the combustion tube which we constructed is shown in Fig. 1, in which a ground glass absorption apparatus for trapping the sulfur is included.

TABLE 3

Designation of Compound and Empirical Formula	Wt. in mg	Weight, in mg			Found %			Difference, %		
		CO_2	H_2O	SO_4	C	H	S	C	H	S
7,13,15-Trimethyl-6-thiostyrene-9(11)-one-17 $C_9H_{28}OS$ Computed %: C-17.95; H-9.27; S-10.52	5.290	14.520	4.470	1.670	74.91	9.45	10.54	-0.04	+0.18	+0.02
	5.130	14.060	4.210	1.585	74.80	9.18	10.31	-0.15	-0.09	-0.21
α-Naphthyldicyclosulfide $C_{20}H_{28}S$ Computed %: C-80.00; H-9.34; S-10.66	4.800	14.060	4.090	1.535	79.94	9.54	10.68	-0.06	+0.20	+0.02
	4.980	14.585	4.240	1.595	79.92	9.53	10.69	-0.08	+0.19	+0.03
Cyclohexyldecylsulfide $C_{16}H_{32}S$ Computed %: C-74.92; H-12.57; S-12.50	6.420	17.090	7.340	2.450	75.20	12.70	12.74	+0.18	+0.22	+0.24
	5.990	-	-	2.270	-	-	12.65	-	-	+0.15
Semicarbazone-2-methylhexahydrothiochromane-4-one $C_{11}H_{19}ON_3S$ Computed %: C-54.74; H-7.93; S-13.28	3.915	7.856	2.846	1.542	54.76	8.13	13.15	+0.02	+0.20	-0.13
	3.820	7.648	2.710	1.520	54.64	7.94	13.28	-0.10	+0.01	0.00
2,2'-Diisobutoxydiethylsulfide $C_{12}H_{26}O_2S$ Computed %: C-61.49; H-11.18; S-13.68	6.833	15.392	6.830	2.790	61.48	11.18	13.63	-0.01	0.00	-0.05
	5.070	11.424	5.074	2.059	61.49	11.20	13.55	0.00	+0.02	-0.13
2,5-Dimethyltetrahydro-1-thiopyral-4-cyanoacetic acid $C_{10}H_{13}O_2NS$ Computed %: C-56.85; H-6.20; S-15.14	5.438	11.362	3.070	2.460	57.02	6.32	15.10	+0.17	+0.12	-0.04
	5.139	10.747	2.938	2.373	57.07	6.40	15.42	+0.24	+0.20	+0.28
The amide of 2,5-dimethyltetrahydrothiopyrane-4-hydroxy-4-acetic acid $C_9H_{17}O_2NS$ Computed %: C-56.16; H-8.43; S-15.77.	4.310	8.400	3.327	2.020	53.19	8.64	15.65	+0.03	+0.21	-0.12
	3.960	7.740	3.028	1.850	53.34	8.56	15.60	+0.18	+0.12	-0.17

Table 3 (continued)

Designation of Compound and Empirical Formula	Wt. in mg	Weight, in mg			Found %:			Difference, %		
		CO_2	H_2O	SO_4	C	H	S	C	H	S
Phenlcyclopentylmercaptan $C_{11}H_{14}S$ Computed %: C-74.10; H-7.92; S-17.98	6.090	16.577	4.332	3.328	74.28	7.96	18.24	+0.18	+0.04	+0.26
	5.297	14.440	3.740	2.840	74.40	7.90	17.90	+0.30	−0.02	−0.08
α-Thionaphthol $C_{10}H_8S$ Computed %: C-74.96; H-5.03; S-20.01	4.200	11.540	1.920	2.525	74.98	5.12	20.07	+0.02	+0.09	+0.06
	4.320	11.860	1.980	2.600	74.92	5.13	20.08	−0.04	+0.10	+0.08
2-Methyl-2-3-dihydrothiopyrane dioxide $C_6H_8O_3S$ Computed %: C-44.98; H-5.03; S-20.02	6.700	11.031	3.035	3.995	44.93	5.07	19.90	−0.05	+0.04	−0.12
	5.598	9.185	2.506	3.345	44.78	5.01	19.95	−0.20	−0.02	−0.07
Bis-β-butoxyethylmercapto-1,1-ethane $C_{14}H_{30}O_2S$ Computed %: C-57.09; H-10.27; S-21.77	4.575	9.550	4.217	3.00	56.84	10.30	21.84	−0.25	+0.03	+0.07
	7.911	15.440	6.827	4.773	57.01	10.34	21.55	−0.08	+0.07	−0.22
Thioxane C_4H_8OS Computed %: C-46.12; H-7.74; S-30.78	4.643	7.850	3.250	4.250	46.14	7.83	30.55	+0.02	+0.09	−0.23
	4.986	8.442	3.460	4.562	46.20	7.76	30.54	+0.08	+0.02	−0.24
Vinylethylsulfide C_4H_8S Computed %: C-54.49; H-9.14; S-36.37	4.447	8.845	3.624	4.830	54.30	9.14	36.25	−0.19	0.00	−0.12
	4.000	8.770	3.550	4.775	54.39	9.03	36.30	−0.10	−0.11	−0.07
Butanedithiol-1,3 $C_4H_{10}S_2$ Computed %: C-39.30; H-8.24; S-52.46	7.190	10.360	5.295	11.300	39.32	8.24	52.46	+0.02	0.00	0.00
	4.420	6.380	3.260	6.920	39.39	8.25	52.30	+0.09	+0.01	−0.16
Dithialane-1,2 $C_3H_6S_2$ Computed %: C-33.93; H-5.69; S-60.38	3.918	4.005	1.950	7.064	34.16	5.57	60.18	+0.23	−0.12	−0.20
	7.655	9.600	3.960	13.500	34.22	5.79	60.23	+0.29	+0.10	−0.15

Both combustion tube and absorption tube were made of transparent quartz.

This type of joint seems to be stable enough in use and ensures that the apparatus is hermetically sealed during combustion. In addition, such a

combustion tube is universal, since in the absence of sulfur in the test compound, the water absorption apparatus can be directly connected by means of a rubber tube to the outlet tube, leading from the ground glass joint of the combustion tube.

This apparatus has been used successfully for over two years in our own laboratory. All experiments were carried out on this apparatus. As we established previously the length of the combustion tube can be shortened to 365 mm and that of the heating zone to 100 mm [5].

The set up for the simultaneous determination of carbon, hydrogen and sulfur is shown in Fig. 2.

The Apparatus for Sulfur Absorption. In constructing this apparatus, Fig. 1, it was borne in mind that it would have to be weighed on a micro balance. The apparatus is provided on one side with an outlet tube of internal diameter 1 mm, and on the other with a ground glass cone, by means of which it can be connected to the combustion tube. When the apparatus is weighed it is sealed by means of a hollow ground glass stopper. This type of construction eliminates the diffusion of external oxygen during weighing. The absorption tube for sulfur is weighed full of oxygen just the same as the absorption tubes for CO_2 and H_2O.

The sulfur absorption tube is filled with metallic silver through the wide opening. It is better to use silver in the form of fine ribbon, turnings or wadding, since in these forms silver has a large surface in relation to a small weight.[1)]

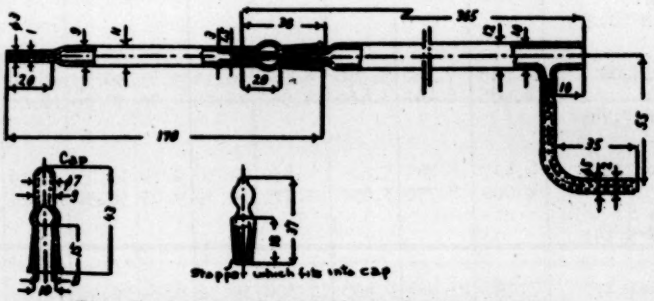

Fig. 1. A new model of the combustion tube

The weight of silver, in the form of ribbon for filling the tube amounted to 2.5-3.5 g. This amount is sufficient for 25-30 sulfur determinations, in the course of which less than a half of the silver is used, and this can be replaced.

Procedure

Before starting a run and while the electric furnaces 1, 7 and 9 (Fig.2) are heated to the requisite temperature, the absorption tube containing the silver is connected by means of its ground glass joint to the combustion tube and a short electric furnace 8-10 cm long which can be heated to 700° fitted on to it. The absorption tubes for water and carbon dioxide are then respectively fitted on and

1) We observed that the activity of the silver can be enhanced before use by reduction with methyl alcohol. The catalytic activity of silver reduced with hydrogen is considerably lower and moreover the silver loses its mechanical stability by hydrogen treatment.

a blank run made. After the blank test all the absorption tubes are weighed, the silver tube being weighed last. The tubes are then all connected up again with the combustion tube, the test sample in its ampoule introduced and combustion carried out as described previously in the method for the determination of carbon and hydrogen [6].

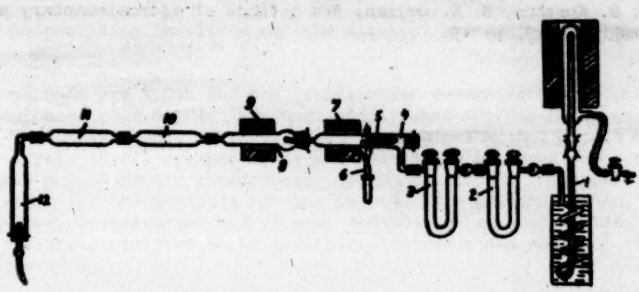

Fig. 2. Set up for the simultaneous determination of carbon, hydrogen and sulfur.

1 - Gas purifying apparatus with electric furnace; 2 - U tube with ascarite; 3 - U tube with anhydrone; 4 - quartz combustion tube; 5 - quartz ampoule for sample; 6 - burner; 7 and 9 - electric furnaces; 8 - sulfur absorption apparatus; 10 - water absorption tube; 11 - carbon dioxide absorption tube; 12 - end tube with anhydrone.

If halides are present as well as sulfur, determination of each of the elements separately is impossible. The presence of nitrogen does not interfere with the simultaneous determination of carbon, hydrogen and sulfur.

We regard it a pleasant task to express our heartfelt thanks to the Docent of the Chair of Petroleum in the Chemistry Faculty of the Moscow State University, I. N. Tits-Skvortsov, who kindly gave me a number of pure compounds for confirmatory work by the method developed.

SUMMARY

1. A new gravimetric method for the simultaneous determination of carbon, hydrogen and sulfur on one aliquot of 4-7 mg has been worked out. The accuracy of determination for the three elements is 0.2-0.3%.

2. The method consists in the decomposition of the sample by the usual method in an empty tube in a rapid stream of oxygen (35-40 ml/min) with subsequent trapping of the products of oxidation by the respective absorbents. Metallic silver is used in a special quartz tube for trapping sulfur oxides. Carbon dioxide and water are trapped as usual by means of ascarite and anhydrone respectively.

3. The optimum temperature for the quantitative absorption of sulfur oxides by silver was found to be in the range 650-800°.

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A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

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Many methods are known for the quantitative determination of nitrogen in organic compounds [3,4,6-10]. The most widely used are the Dumas and Kjeldhal methods. The Dumas method is regarded as a classical method and is applied for the analysis of all organic materials containing nitrogen. The drawbacks of the Dumas method are its awkwardness, the complexity of the apparatus, and the time taken for one analysis by this method. The Kjeldhal method is widely used in factory laboratories and in some scientific-research institutes, because it enables several analyses to be made simultaneously and does not require complex apparatus.

The drawback of the Kjeldhal method is its limited field of application.

Kjeldhal's method can only be used with difficulty for the analysis of nitro-, nitroso-, azo-compounds and particularly of heterocyclic nitrogen compounds.

A new method which we have developed for the quantitative determination of nitrogen in any organic compound is described in the present article. The principle of this quantitative determination of nitrogen in organic compounds is the heating of the nitrogenous compound in an atmosphere of hydrogen with magnesium powder [1,2,5]. Under these conditions the nitrogen reacts quantitatively with the magnesium to form magnesium nitride, which on decomposition with water yields ammonia. The latter is distilled over into a standard acid solution and determined quantitatively.

The reaction between magnesium and an organic compound containing nitrogen is carried out in a test tube or glass tube. On heating, the magnesium partly reacts with the glass, forming an insignificant amount of magnesium silicide, from which on further treatment of the reaction mass with acid, gaseous, easily inflammable silicon hydride is formed. If however the reaction mass is treated with water the inflammable silicon hydride is hardly formed at all. The slight explosions which sometimes occur at the beginning of the water treatment, do not affect the accuracy of the analysis.

Magnesium powder under our experimental conditions reacts easily not only with the nitrogen of the organic compounds, but also with halogens or sulfur. This enables nitrogen, halogens and sulfur to be determined simultaneously on one aliquot. Work is in progress on these lines. It is possible to carry out 4-5 analyses in one apparatus in one day. The time required for one analysis is 1.5 hours, the accuracy being of the order of 0.2-0.3%.

EXPERIMENTAL

About 0.1-0.15 g of the organic compound is introduced into the test tube and a small layer of magnesium powder (1.5-2 cm) spread over it.

A thin glass tube a is then fixed in the tube, a does not reach right down to the bottom. More magnesium powder is then introduced almost up to the cork. A short glass tube b, the diameter of which is slightly greater than the

diameter of tube a, is fitted into the hole of the cork. The closed test tube is turned upside down and the tube a projecting from it connected with a Kipps apparatus.

Liquids for analysis are introduced in glass ampoules.

The air is expelled from the apparatus by a stream of hydrogen in the course of 10-15 minutes. After 15 minutes while the hydrogen is still being passed, the tube a is carefully removed from the test tube, and the Kipps disconnected. A rubber tube with clips at its ends and filled with water is fitted on to tube b. The tube is filled with water to exclude aerial nitrogen from the reaction tube. The test sample is then carefully shaken so as to mix it with the magnesium. The clips on the rubber tube are opened 1-2 minutes after switching on the combustion furnace and closed after the reaction has stopped. Heating can be carried out with a gas burner.

In our work we used a specially constructed electric furnace the general features of which are shown in Fig. 2.

Fig. 1. Test tube. 1) Sample. 2) first layer of magnesium 2') magnesium. a] Glass tube for passing hydrogen; b] glass tube for expulsion of gases.

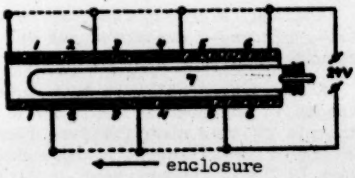

Fig. 2. Set up for electric furnace 1,2,3,4,5 and 6 - sections of the electric furnace; 7 - test tube.

The furnace consists of 4-6 sections, which can be switched on in stages. Such a set up enables the heating zone to be increased gradually as it approaches the test material.

The test tube should not be heated higher than a dark red heat (600-650°). Most organic compounds decompose completely on switching on the first two sections of the furnace (5-6 cm) at a dark red heat.

If evolution of gas is slow, the rate of heating can be increased by switching on the next section of the furnace. The combustion process can be followed by the rate of evolution of gas formed in the apparatus during decomposition of the organic compound (Fig. 3). This is achieved by immersing the rubber tube leading from the test tube in water under a cylinder or by leading it into a crystallizing basin with water.

Combustion may be regarded as complete several minutes after all the test tube has been heated to a dark red. The evolution of gas bubbles at this stage becomes very slow. Combustion should last 25-30 minutes. The test tube is cooled carefully, and broken as quickly as possible in a mortar and transferred to a 500-800 ml round-bottom flask. In order to decompose the magnesium nitride

completely 20-25 ml of 10% sulfuric acid is added. The silicon hydride which is evolved on addition of acid can ignite in the presence of air and lead to an explosion of the mixture of hydrogen and aerial oxygen. It is essential therefore that the air be expelled with carbon dioxide before addition of acid. An excess of strong alkali is finally added and the ammonia distilled over into a definite volume of standard 0.1 N hydrochloric or sulfuric acid. Distillation of the ammonia takes 30-35 minutes. Excess acid is titrated with 0.1 N alkali using methyl orange as an indicator and the nitrogen content calculated.

The results given in the table show that the accuracy is sufficient for the determination of nitrogen in organic compounds.

TABLE 1

No.	Compound tested	Molecular Formula	Calculated N,%	Found N,%	Difference
1	Nitrobenzene	$C_6H_5NO_2$	11.38	11.23	−0.15
			11.38	11.19	−0.19
2	o-Nitrotoluene	$C_7H_7NO_2$	10.21	10.03	−0.18
			10.21	10.14	−0.07
3	Nitrophenol	$C_6H_5NO_3$	10.07	10.01	−0.06
			10.07	9.77	−0.30
4	o-Nitroanisole	$C_7H_7NO_3$	11.56	11.37	−0.19
			11.56	11.36	−0.20
5	Aniline	C_6H_7N	15.04	14.85	−0.19
			15.04	15.32	+0.28
6	Toluidine	C_7H_9N	13.07	13.28	+0.21
			13.07	13.08	+0.01
7	Dimethylaniline	$C_8H_{11}N$	11.56	11.30	−0.26
			11.56	11.75	+0.19
8	Diphenylamine	$C_{12}H_{11}N$	8.28	8.25	−0.03
			8.28	8.31	+0.03
9	m-Nitraniline	$C_6H_6N_2O_2$	20.28	20.05	−0.23
			20.28	19.90	−0.30
10	p-Nitraniline	$C_6H_6N_2O_2$	20.28	20.40	+0.12
			20.28	20.38	+0.10
11	o-Nitro-p-toluidene	$C_7H_8N_2O_2$	18.41	18.15	−0.26
			18.41	18.40	−0.01
12	Ethylaniline	$C_8H_{11}N$	11.56	11.49	−0.07
			11.56	11.69	+0.09
13	Diphenylthiourea	$C_{13}H_{12}N_2S$	12.27	12.32	+0.05
			12.27	12.28	+0.01
14	Sulfanilic acid	$C_6H_7NO_3S \cdot H_2O$	6.69	6.40	−0.29
			6.69	6.52	−0.17
15	Naphthenic acid	$C_{10}H_9NO_3S$	6.27	5.98	−0.29
			6.27	6.16	−0.11
16	Azobenzene	$C_{12}H_{10}N_2$	15.37	15.24	−0.17
			15.37	15.36	−0.10

SUMMARY

1. A method is described for the quantitative determination of nitrogen in any organic compound, which is based on heating the compound with magnesium powder in an atmosphere of hydrogen.

2. The analysis is carried out in ordinary glass test tubes. One analysis takes 1.5 hours, so that 5-6 analyses could be carried out in a working day. The accuracy of the method is 0.2–0.3%.

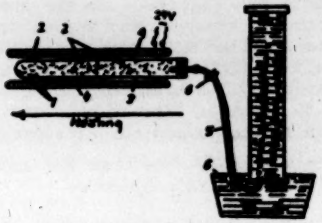

Fig. 3
1) Sample; 2) magnesium; 3) test tube; 4) furnace; 5) rubber tube; 6) clips.

3. The results obtained by the above method give us grounds for hoping that it will be widely used.

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A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF SULFUR, AND FOR THE SIMULTANEOUS DETERMINATION OF SULFUR AND NITROGEN IN ORGANIC COMPOUNDS

P. N. Fedoseev and N. P. Ivashova

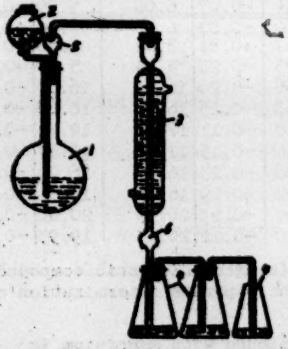
(Nikolaev Shipbuilding Institute and the Nikolaev Pedagogic Institute)

In our first paper [1] we showed that all the nitrogen in an organic compound is quantitatively converted on heating with metallic magnesium powder at 550-650° into magnesium nitride [2-10].

In this article a method is described for the determination of sulfur, and also for the determination of nitrogen and sulfur on one aliquot by the same principle. For the quantitative determination of sulfur in organic compounds, the compound is heated with magnesium powder at 550-650° for 30-40 minutes. All forms of organically bound sulfur are thus quantitatively converted into magnesium sulfide. The combustion of the organic sulfur compounds is carried out in an ordinary glass test tube. Nitrogen can also be determined simultaneously with sulfur [1]. In this case magnesium nitride and magnesium sulfide respectively are formed. On acid treatment an ammonium salt and hydrogen sulfide are formed. The hydrogen sulfide is determined iodometrically and by addition of strong alkali to the flask after removal of the hydrogen sulfide, the ammonia can be distilled over into standard acid solution and determined by back titration of the excess acid with alkali.

Combustion (30-35 minutes) of an aliquot of the test compound is carried out as described in the previous article. The test tube and its contents are ground up and transferred to a 500 ml round bottom long necked flask containing 50-80 ml of distilled water.

A stream of carbon dioxide is passed through the apparatus (see diagram) in order to expel the air, in the presence of which, on addition of acid, an explosive mixture can be formed which can be ignited by the silicon hydride (which is inflammable in the presence of air). Air will also favor the oxidation of hydrogen sulfide. When the air has been expelled, a small excess (80-100 ml) of 12% hydrochloric acid is gradually added to the flask used for decomposition so as to dissolve the remainder of the magnesium and the magnesium sulfide. A large part of the hydrogen sulfide is expelled together with the hydrogen formed and is mainly absorbed in the first absorption flask, which contains 65 ml of a mixture of 10% $ZnSO_4$ and 10% CH_3COONa with 3-5 ml of concentrated acetic acid.



Apparatus for expelling air with CO_2: 1) distillation; flask; 2) dropping funnel 3) condenser; 4)receivers; 5) splash head; 6) safety space.

The second and third absorption flasks contain 50 and 25 ml of the same mixture respectively. After all (or almost all) the magnesium has dissolved, the flask is heated for 20-25 minutes to drive over any residual hydrogen sulfide with steam. In all 70-80 ml of liquid is distilled over. When all the hydrogen sulfide has been driven over, 25 ml of 0.1 N iodine is added to the contents of the

first two absorption flasks and acidified with a few drops of 12% hydrochloric acid. After standing for three minutes the excess iodine is titrated with thiosulfate.

Results of the determination of sulfur in a number of organic compounds are given in Table 1. They show that the analytical error lies within the range 0.2–0.3%.

TABLE 1

Molecular Formula of Compound and Designation	S %			N %		
	Computed	Found	Diff.	Computed	Found	Diff.
Sulfosalicylic acid ($C_7H_6SO_6 \cdot 2H_2O$)	12.61	12.71	+0.10			
	12.61	12.69	+0.08			
Sodium alizarinsulfonate ($C_{14}H_7O_7SNa$)	9.37	9.20	−0.17			
	9.37	9.27	−0.10			
Sodium p-toluenesulfonate ($C_7H_7O_3SNa \cdot 2H_2O$)	13.92	13.65	−0.27			
	13.92	13.63	−0.29			
Bis-(1,1-dimethylpentene-3-one-sulfide ($C_{14}H_{24}O_2S$)	12.60	12.50	−0.10			
	12.60	12.54	−0.06			
Acetothienone (C_6H_6OS)	25.25	25.28	+0.03			
	25.25	25.21	−0.04			
Ditolylsulfide ($C_{14}H_{14}S$)	14.96	14.81	−0.15			
	14.96	14.69	−0.17			
Naphthenic acid $\left(C_{10}H_9NSO_3 \cdot \frac{1}{2} H_2O\right)$	13.81	14.04	+0.23	6.03	6.13	+0.10
	13.81	13.75	−0.06	6.03	6.16	+0.13
Sulfanilic acid ($C_6H_7O_3SN \cdot 2H_2O$)	15.32	15.30	−0.02	6.69	6.50	−0.19
	15.32	15.11	−0.21	6.69	6.73	+0.04
p-Toluenesulfamide ($C_7H_9SO_2N$)	18.72	17.51	−0.21	8.18	7.98	−0.20
	18.72	18.48	−0.24	8.18	7.89	−0.29
o-Toluenesulfamide ($C_7H_9SO_2N$)	18.72	18.56	−0.16	8.18	8.00	−0.18
	18.72	18.53	−0.19	8.18	8.01	−0.17
Diphenylthiourea ($C_{13}H_{12}N_2S$)	14.04	14.23	+0.19	12.27	11.98	−0.29
	14.04	14.15	+0.11	12.27	11.99	−0.28
p-Methoxyphenyl-pseudohydantoic acid ($C_{10}H_{12}O_3N_2S$)	13.34	13.16	−0.18	11.66	11.86	+0.20
	13.34	13.39	+0.05	11.66	11.66	0.00
Sodium sulfanilate ($C_6H_6NSO_3Na \cdot 2H_2O$)	13.87	13.94	+0.07	6.06	5.90	−0.16
	13.87	13.80	−0.07	6.06	5.96	−0.10
N-Methylbenzanilide-o-methylsulfide ($C_{15}H_{15}SNO$)	12.46	12.67	+0.21	5.44	5.30	−0.14
	12.46	12.23	−0.23	5.44	5.59	+0.15
2-(p-aminobenzenesulfamidopyridine) ($C_{11}H_{11}O_2N_3S$)	12.86	12.66	−0.20	16.85	16.60	−0.25
	12.86	12.63	−0.23	16.85	16.68	−0.17
4-Sulfanilylsulfanilamide ($C_{12}H_{13}O_4N_3S_2$)	19.59	19.48	−0.11	12.83	12.74	−0.09
	19.59	19.44	−0.15	12.83	12.67	−0.16
2-(p-Aminobenzenesulfamidothiazole) ($C_9H_9O_2N_3S$)	25.11	24.88	−0.23	16.46	16.26	−0.20
	25.11	25.02	−0.09	16.46	16.34	−0.12
2-Sulfanilamido-4,6-dimethylpyrimidine ($C_{12}H_{14}O_2N_4S$)	11.52	11.29	−0.23	20.13	20.00	−0.13
	11.52	11.40	−0.12	20.13	19.93	−0.20

For simultaneous determination of sulfur and nitrogen in organic compounds, combustion is carried out in the same way as for the separate determination of sulfur and nitrogen [1].

The residue after combustion of the organic compound with magnesium is transferred into a flask for decomposition. It is recommended that the sulfur be determined first by the method and in the apparatus described already (Fig.2).

When the hydrogen sulfide has been removed, the receivers for the hydrogen sulfide are removed and flasks containing standard acid (hydrochloric or sulfuric acids) for absorption of the ammonia substituted instead. The condenser and Kjeldhal set up are washed out while the two sets of flasks are being interchanged. Finally by means of a separating funnel, 50-60 ml of 50% alkali is added to the contents of the flask and the ammonia distilled over.

Results for simultaneous determinations of sulfur and nitrogen are given in Table 1.

In addition we determined total sulfur in a number of coal samples, kindly given us by the Moscow All Union Scientific Research Thermo-Technical Institute, for which we wish to express our thanks to the chief of the Heat Laboratory of the Institute, Comrade Zikeev. The results which are given in Table 2 show that our method is suitable for the quantitative determination of sulfur in coal.

TABLE 2

Coal Used	% S found in the Labs. of VTI[1])	% S found in the Labs. of NKI[2])	Diff.	No. of the VTI[1]) Analysis
Coal "T"	2.93 2.93	2.79 2.65	-0.14 -0.28	5617
Podmoscovni	3.48 3.48	3.30 3.25	-0.18 -0.23	5771
Silesian	2.23 2.23	2.04 2.98	-0.19 -0.25	5753 -
Coal "PS"	0.98 0.98	0.95 0.86	-0.03 -0.12	5640
Anthracite "ARSh"	1.93 1.93	1.64 1.68	-0.29 -0.24	5644
Komarovsk (Podmos.)	4.98 4.98	4.95 4.94	-0.03 -0.04	6364
Angrensk	2.70 2.70	2.73 2.80	+0.03 +0.10	6694
Donets	5.14 5.14	5.27 5.02	+0.13 -0.12	6372
Anthracite "ARSh"	4.35 4.35	4.46 4.51	+0.11 +0.16	4907
Brown Coal Dust	1.68 1.68	1.65 1.60	-0.05 -0.08	6545

1) VTI - F. E. Dzerzhinskov All Union Scientific-Research Thermotechnical Institute.
2) NKI - Admiral S. O. Makarova Nikolaev Shipbuilding Institute.

SUMMARY

1. A quantitative method for the determination of sulfur and for the simultaneous determination of nitrogen and sulfur in organic compounds is proposed.

2. The accuracy of the method lies in the range ± 0.2 – 0.3%. The results of analyses gives grounds for hoping that the given method may be used in a number of scientific-research and factory laboratories. Comparative results for the determination of total sulfur in different samples of coal carried out by the authors and the All Union Scientific Research Institute, give good agreement.

3. The method of determination is simple, generally applicable, does not require complicated apparatus, and gives reliable results.

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SALICYLALAMINES IN ANALYSIS

4. TRICYCLIC INNER COMPLEX SALTS OF COPPER AND NICKEL

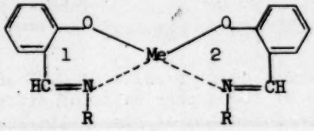
A. P.Terentyev, E. G. Rukhadze and Z. A. Fadeeva

(Lomonosov Moscow State University)

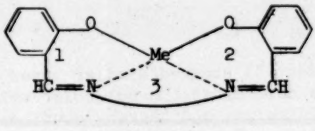
In previous papers [1] we considered the changes in the physico-chemical parameters and analytical properties of a series of Cu^{2+} and Ni^{2+} salts of the simplest homologs of the salicylalalkyl amines. The structure of the "analytical junction" in the metallic derivatives of these compounds remains unchanged, as was to be expected for the homologs. Physico-chemical properties change uniformly. The analytical character also changes very little basically.

In the present paper we shall consider the changes in the analytical parameters as a result of the effect of radical regrouping of the "analytical junction". By the term "analytical junction" we mean that system of atoms which is made up from the specific groups of molecules of the reagent and the atoms or atoms of the metal to be determined [2].

The compounds under consideration are the condensation products of salicylaldehyde with aliphatic and aromatic diamines-disalicylaldiamines. These compounds form "analytical junctions" with bivalent metals, which are composed of three mutually connected metal-rings (II) and not two rings as was the case with salicylalmonoamines (I)

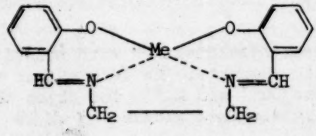


I

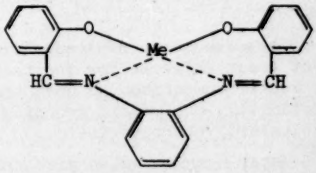


II

The effect, in the first place, of the valency structures, and secondly of the stereochemical characteristics of this third ring can become manifest to its fullest extent only during the formation of a complete analytical form. The first, obviously, is most clearly shown on comparison of the properties of the inner complex salts of Cu^{2+} and Ni^{2+} for disalicylalethylenediamine on the one hand (III) and for disalicylal-o-phenylendiamine (IV) on the other.



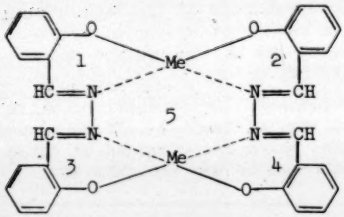
III



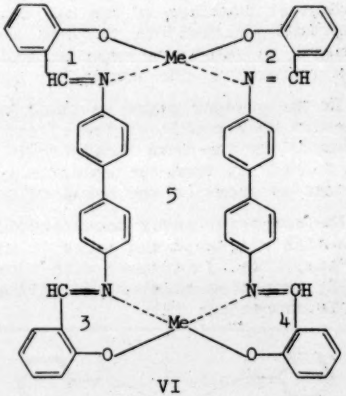
IV

The interaction between the original rings will be greater in the case of (IV) with an unbroken system of strained bonds than in the case of (III). One would expect a considerable difference in similar systems with regard to their stability, fusibility, solubility and particularly color.

The stereochemical effect could be manifested during attempts to form the third ring of the "analytical junction" as a sterically "awkward" system. Thus disalicylalazine, the reaction product of salicylaldehyde and hydrazine, should form an "analytical junction" with highly strained three-membered rings with Cu^{2+} or Ni^{2+}. The existence of a simple ring for salts of disalicylal-p-phenylenediamine and disalicylalbenzidene is impossible. In these cases one would expect the formation of a double system of a complex five-ring junction with two metal atoms (V,VI).



V



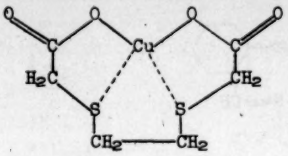
VI

Pfeiffer [3] studied similar types of inner complex salts of Cu^{2+} and Ni^{2+} in 1936; he determined the molecular weights of the copper salts of different disalicylaldiamines and thereby confirmed the formation of bimetallic five membered rings. For the syntheses of these inner complex salts it is natural to use an excess of the metal salt; when analytical precipitation is carried out, the formation of the complex salt proceeds under conditions where there is a deficiency of metal ions, since an excess of the reagent-precipitant is used. When using disalicylaldiamines therefore, as reagents, it would be natural to expect anomalies in the quantitative composition and the character of the precipitates. It is obvious that monometallic (i.e. containing one metal atom) "incomplete" molecules will be present and not only dimerization, but linear polymerization, which is so characteristic for "long" molecules, will occur. In this case this will be reflected in the character of the precipitate – mucilegenous instead of crystalline.

Thus the study of the interaction of disalicylaldiamines with metallic ions is of great interest for the theory of organic reagents. As in previous work, for better comparison we used the same cations Cu^{2+} and Ni^{2+}, for which the functionally-analytical grouping of the salicylalamines studied by us is particularly characteristic.

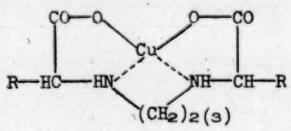
Inner complex salts with three mutually connected metal rings have been known for a long time. In 1916, Tiberg [4] prepared a number of the tricyclic

salts of Cu^{2+}, Cu^{+}, Pt^{2+} and Ag^{+}. The neutral copper salt of ethylenethioglycolic acid (VII), which is prepared by the action of sodium ethylenthioglycolate on an aqueous solution of a copper salt is a typical example of these salts.



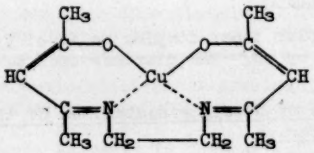
VII

Shlezinger [5] obtained various salts of ethylene and trimethylene-α-imino acids. All these salts have the following structure (VIII):



VIII

Morgan and Smith [6] by the action of acetylacetone and ethylenediamine on salts of Cu^{2+} and Co^{2+} obtained the ethylendiamino biacetylacetonates of copper and cobalt (IX):

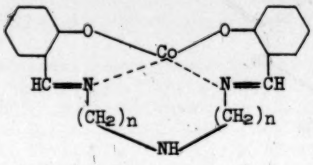


IX

Pfeiffer and coworkers [7] made more profound and wider studies of the properties of these tricyclic inner complex salts. Compounds of this type were prepared by Pfeiffer from the condensation products of salicylaldehyde with aliphatic diamines of the type $NH_2(CH_2)_nNH_2$ (n = 2-10); numerous tricyclic salts were thus prepared. In accordance with stereochemical multichain rings can be formed, when the links in the system consist of mobile chains of $-CH_2$ which can withstand bending (are pliable). In the case of aromatic diamines, where mobility is absent on account of the planar structure of the aromatic nucleus, monometallic systems can only be formed by orthodiamines. Para-diamines of the type of paraphenylenediamine and benzidene can yield only more complex inner complex salts with two metal atoms. It should be noted that according to Pfeiffer's results, all of this tricyclic system with bivalent metals is in one plane.

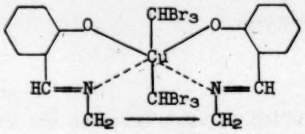
Tricyclic inner complex salts have found practical application in recent years. Thus in 1946, Calvin [8] showed that copper and zinc salicylal-o-phenylendiamines show a high specificity for neutrons. By bombardment of copper salicylal-o-phenlyendiamine with neutrons, it is possible to separate copper from other isotopes. It was also found [8] that a Co^{2+} salt of the type (X) can

combine reversibly with aerial oxygen. Such cyclic coordinately-saturated complexes should play an important part in biological oxidation-reduction processes.



(X)

Organic reagents which form tricyclic inner complex salts have not been accepted in analytical chemistry practice. There is one reference [9] to the use of a compound (XI) in luminescence analysis.



(XI)

EXPERIMENTAL

Monometallic and bimetallic tricyclic inner complex salts of Cu^{2+} and Ni^{2+} with disalicylaldiamines were isolated by us. The diamines used were of the aliphatic and aromatic series.

1. Monometallic Tricyclic Systems of Disalicylaldiamines of the Aliphatic Series

Disalicylalethylenediamine was prepared by the normal method – reaction of salicylaldehyde with ethylenediamine in the ratio 2:1 [2]. This yellow crystalline compound has a melting point of 125° and is soluble in acetone and alcohol. 1.5% solutions of disalicylalethylenediamine in alcohol or acetone precipitate Cu^{2+} in the form of green crystals and Ni^{2+} in the form of yellow-orange crystals.

Disalicylalpropylenediamine is a thick yellow oily liquid; it is soluble in alcohol, ether and acetone. A 1% alcoholic solution of disalicylalpropylenediamine precipitates Cu^{2+} in the form of a violet amorphous precipitate; and Ni^{2+} gives yellow-orange needle-like crystals.

The tricyclic monometallic salts of Cu^{2+} and Ni^{2+} with disalicylalethylendiamine and disalicylalpropylenediamine differ considerably from the salicylalmonoamines [1] in their physico-chemical and analytical parameters.

Melting Point. The tricyclic salts of Cu^{2+} and Ni^{2+} have high m.p's. They melt with decomposition above 200°. They differ considerably in this respect from the salicylalamines, which have lower melting points and are often oily [1].

Solubility. All the salts dissolve readily in organic solvents: pyridine, ethyl ether, ethyl acetate, chloroform, carbon tetrachloride, benzene, isoamyl alcohol, etc. The solubility of the higher homolog is considerably higher. The solutions are colored – the copper salts are either green (disalicylalethylene-

diamine salt) or violet (disalicylalpropylenediamine salt), while the nickel salts are orange-yellow. The color of the diamine salts is considerably more intense than those of the monoamines.

The solubility of the Cu^{2+} and Ni^{2+} salts in water is considerably greater than that of the respective complex monoamine salts. For comparison the solubilities of the complex salts of Cu^{2+} and Ni^{2+} with disalicylalpropylenediamine are given below.

TABLE 1

Solubility of the Cu^{2+} and Ni^{2+} Salts of Salicylalpropylenediamine

The amine condensed with salicylaldehyde	Solubility in 100 g water in mg	
	Cu^{2+}	Ni^{2+}
Propylenediamine	7.17	1.93

Sensitivity to pH. The Cu^{2+} and Ni^{2+} salts of the tricyclic derivatives of the diamines studied differ from the corresponding salts of the monoamines by their considerably greater stability to acids and bases. Thus the former are not decomposed by 0.01 N CH_3CO_2H, 0.01 N HCl, or by strong solutions of NaOH and NH_4OH. Salicylalmonoamines of Cu^{2+} and Ni^{2+} as a rule, are less stable to dilute acids and strong alkalies; the pH for precipitation of the disalicylalethylenediamines of Cu^{2+} and Ni^{2+} is 7.2, and for the disalicylalpropylenediamines of Cu^{2+} and Ni^{2+} - 6.8.

2. Monometallic Tricyclic Systems of the Disalicylaldiamines of the Aromatic Series

Disalicylal-o-phenylenediamine is easily prepared by mixing alcoholic solutions of salicylaldehyde and o-phenylenediamine in the ratio 2:1. The mixture is heated for one hour in a flask with an air condenser on a water bath. After cooling, yellow needles separate out which have a m.p. of 164°. They are soluble in alcohol, ether and benzene.

A 1% alcoholic solution of disalicylal-o-phenylendiamine precipitates Cu^{2+} in the form of an intensely brown colored precipitate; salts of Ni^{2+} with this amine are bright red needle-like crystals. Both salts dissolve readily in the ordinary organic solvents to form brightly colored solutions. The colors of solutions of the disalicylaldiamines of the aromatic series are far more intense than those of the disalicylaldiamines of the aliphatic series. The copper salt is stable to 0.01 N CH_3CO_2H and to both dilute and strong alkalies; the precipitation pH is 5.7. The nickel salts are less stable and are decomposed by dilute acids and strong alkalies - the precipitation pH is 8.0.

3. Bimetallic Systems of the Disalicylaldiamines

Disalicylalazine is obtained by the usual method from salicylaldehyde dissolved in alcohol and hydrazine hydrate (a 40% aqueous solution) in the ratio 2:1; this compound exists as colorless lustrous crystals in the form of platelets with a m.p. of 98°; it dissolves in alcohol, ether and other organic solvents.

A 1% alcoholic solution of disalicylalazine rapidly and quantitatively precipitates Cu^{2+} in the form of pale-yellow, and Ni^{2+} as yellow crystalline precipitates. As stated above disalicylalazine should form a bimetallic system with five rings. The "analytical junction" of this salt contain a strainless six membered ring, which explains its ease of formation and the considerable stability of these inner complex salts.

Cu^{2+} and Ni^{2+} disalicylalazines do not change even on heating above 150°. The m.p. (with decomposition) of the Cu^{2+} salt is 258° and of the Ni^{2+} salt 350°. Both salts are insoluble in the usual organic solvents. 1.2 mg of the Cu salt

and 0.59 mg of the Ni salts, respectively, dissolve in 100 ml of water at ordinary temperatures; the pH for precipitation of the Cu^{2+} and Ni^{2+} disalicylalazines is 7-8.

Disalicylal-m-Phenylenediamine, Disalicylal-p-Phenylenediamine, and Disalicylalbenzidene are prepared in the same way as disalicylal-o-phenylenediamine. They are solid crystalline compounds. Disalicylal-m-phenylenediamine consists of dark yellow needles - m.p. 105°; disalicylal-p-phenylenediamines of orange red needles - m.p. 210°; disalicylalbenzidine of yellow green powder - m.p. 256°. All these compounds are only slightly soluble in water but dissolve in alcohol and benzene. Alcoholic solutions of these disalicylaldiamines precipitate Cu^{2+} and Ni^{2+}, but these precipitates differ from the usual ones in their external appearance - being non-crystalline and mucilagenous. Precipitation is not quantitative. Well formed inner complex salts of Cu^{2+} and Ni^{2+} with these reagents can only be prepared by taking a considerable amount of the respective neutral salt. This indicates that only in such a case is it possible to get more suitable conditions for the formation of double, bimetallic systems.

Practical Application of Disalicylaldiamines

Disalicylalethylenediamine, disalicylal-o-phenylenediamine, disalicylalazine are of no practical interest as reagents for the quantitative determination of copper, since the low solubility of these reagents often leads to high results. Nickel can be quantitatively precipitated by these reagents only in a very narrow pH range. Disalicylalpropylenediamine can however be recommended for the quantitative determination of Cu^{2+} and Ni^{2+}.

Reagent. 1) 1% alcoholic solution of disalicylalpropylenediamine and 2) a 10% solution of sodium acetate.

Determination of Copper

To a solution containing 5-25 mg Cu, 3-4 drops of methyl red or bromothymol blue are added, and 10% sodium acetate added until a yellow (or blue) color respectively is obtained. A 1% alcoholic solution of disalicylalpropylenediamine is then added dropwise with stirring; a violet precipitate is formed. The mixture is diluted to 100 ml with water and after standing for six hours, it is filtered through a filter crucible of average density. The precipitate is washed with cold water and dried at 130°. Correction factor 0.1848 (log 1, 26,670. Calculated molecular weight 343.8.

Results for determination of copper are given in Table 2.

TABLE 2

Determination of Copper with Disalicylalpropylenediamine

Expt. No.	Cu^{2+} taken in mg	Wt. Ppt. mg	Cu^{2+} found mg	Error mg	Error %
1	24.57	0.1329	24.56	-0.01	0.04
2	9.82	0.0530	9.79	-0.03	0.3

Analysis of copper disalicylalpropylenediamine

5.180 mg substance: 0.374 ml N_2 (23°, 748 mm)
5.480 mg substance: 0.399 ml N_2 (22°, 748 mm)
Found %: N 8.20; 8.29
$C_{17}H_{16}N_2O_2Cu$. Calculated %: N 8.15

Determination of Nickel with Disalicylalpropylenediamine

A solution containing 5-25 mg Ni^{2+} is diluted to 100 ml with water, 10-15 ml of a 10% sodium acetate solution (the color for a bromothymol-blue indicator should be pale blue) added and the mixture brought to the boil. A 1% alcoholic solution of disalicylalpropylenediamine (it is best to make a solution in methyl alcohol) is added dropwise with stirring. Orange-yellow lustrous needles are precipitated immediately. The solution is heated for a further 10-15 minutes and after standing for 3-8 hours it is filtered through a filter crucible of average density,

washed with water and dried at 110-120°. The calculating factor is 0.1731 (log $\bar{1}$, 23830). The computed molecular weight is 339.00.

Results for nickel determinations are given in Table 3.

TABLE 3

Determination of Nickel with Disalicylalpropylenediamine

No.	Ni^{2+} taken in mg	Wt. Ppt. in g	Ni^{2+} Found in mg	Error	
				in mg	in %
1	24.43	0.1384	23.96	-0.47	1.8
2	12.21	0.0692	12.15	-0.06	0.49
3	9.77	0.0562	9.73	-0.04	0.40
4	6.10	0.0350	6.06	-0.04	0.66

Analysis of Nickel Disalicylalpropylenediamine

6.440 mg substance: 0.483 ml N_2 (22°, 752 mm)
4.720 mg substance: 0.350 ml N_2 (21°, 754 mm)
Found %: N 8.59, 8.54.
$C_{17}H_{16}N_2O_2Ni$. Calculated %: N 8.26.

Small amounts of Ni^{2+}, 1 - 0.1 mg, can be determined colorimetrically by means of a standard scale.

Reagents 1) a 1% solution of disalicylalpropylenediamine in methyl alcohol; 2) 10% sodium acetate; 3) a standard $NiSO_4$ solution - 1 ml of which contains 1 mg Ni^{2+}; 4) isoamyl alcohol (the fraction boiling point 128-130°).

Preparation of the Scale

Aliquots of the nickel solution containing 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; and 1 mg of Ni^{2+} respectively are introduced into colorimeter tubes of 70-80 ml capacity and diluted with water to 50 ml, 1.5 ml of the sodium acetate solution, 1 ml of the 1% reagent solution are added to each tube. The tubes are heated in a water bath for 15-20 minutes and then cooled with water. 5 ml of the isoamyl alcohol is added from a burette to each tube, which is then shaken and allowed to stand so that two layers separate out. Test solutions are treated in exactly the same way and the colors developed compared with the standards in direct light.

It should be noted that Co^{2+} is not precipitated by disalicylalpropylenediamine, but forms a light brown compound which is soluble in water from which it is not extracted by isoamyl alcohol.

SUMMARY

1. The changes in the analytical parameters of salicylalamines in relation to their structure and configuration of the "analytical junction" of the inner complex salts of Cu^{2+} and Ni^{2+} have been studied.

2. A number of the condensation products of salicylaldehyde with aliphatic and aromatic diamines and with hydrazine has been prepared.

3. According to the structure of the "analytical junction" these compounds form inner complex salts containing one or two metal atoms with Cu^{2+} and Ni^{2+}. The "analytical junction" of the compounds formed contains three rings (for a complex containing one metal atom) or five rings (for a complex containing two metal atoms).

4. The physico-chemical properties and the analytical character of salts of Cu^{2+} and Ni^{2+} with disalicylalazine, disalicylalethylenediamine, disalicylalpropylenediamine, and disalicylal-o-phenylendiamine, have been studied.

5. Disalicylalpropylenediamine can be used for the quantitative determination of Cu^{2+} and Ni^{2+} gravimetrically, and for small amounts colorimetrically.

6. It has been established that the tricyclic inner complex salts of Cu^{2+} and Ni^{2+} - products of condensation of salicylaldehyde with diamines - are distinguished by their considerably higher stability as compared with the corresponding salts of salicylalmonoamines.

Received July 22, 1949

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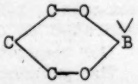
A NEW GROUP OF REAGENTS FOR BORIC ACID

I. M. Korenman and F. R. Sheyanova

(Gorky State University)

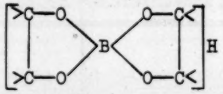
One of us has shown previously [1] that the common property of all known organic reagents for boric acid is the capacity to form inner complex compounds with six membered rings:



Such reagents for boric acid as hydroxyanthraquinone and curcumin, which have been known for some time, possess this capacity. Rings of this type can also be postulated for derivatives of salicylic acid, which can act as reagents for boric acid. This has been confirmed experimentally [1].

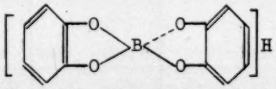
In another paper [2] it was shown that the removal of one of the atoms from the six-membered ring sometimes does not lead to a loss of the respective analytical property (i.e. of acting as a reagent for boric acid). On applying these considerations to reagents for boric acid, it can be postulated that organic compounds which lead to the formation of five membered inner complex rings of the type:

should also possess the capacity to react with boric acid. We have found references in the literature to the possibility of forming such rings. In Glebovich's article [3] the esters of boric acid with polyhydroxy compounds, to which the composition:



is assigned, are noted.

Such rings are also possible for pyrocatechol-boric acid [4] the composition of which is $[(C_6H_4O_2)_2B]H$, and to which the following structural formula can be assigned:

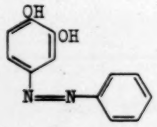
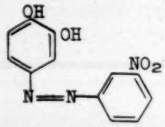
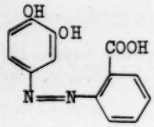
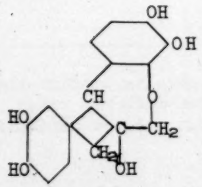


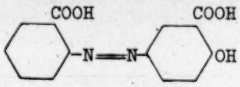
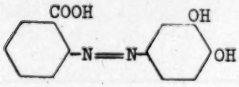
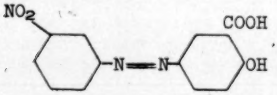
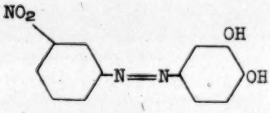
Here we have two five-membered rings. These results confirm that boron (boric acid) is capable of forming not only six- but five-membered rings. Of course pyrocatechol is not a reagent for boric acid, but colored derivatives of

pyrocatechol might be used as reagents. It should be noted that some colored derivatives of pyrocatechol have already been the subjects of research as potential analytical reagents. Kuznetsov [5] in a number of investigations used them for reactions with aluminum, gallium, thorium, zirconium, titanium, antimony and others, nevertheless the capacity of such compounds to give analytical reactions with boric acid had not hitherto been mentioned. Consequently we examined the behavior of some colored derivatives of pyrocatechol with boric acid.

After a number of preliminary tests we finally adopted the following procedure: 1-2 drops of a boric acid solution were placed in a small crucible, and 2 drops of concentrated ammonium hydroxide added to neutralize any strong mineral acids which may be present in large amounts. 1-2 drops of hydrochloric acid (1:1) was then added and the mixture evaporated to dryness on a sand bath. One drop of a saturated alcoholic solution of the reagent was added to the dry hot residue and again evaporated to dryness. The presence of boric acid is indicated by the appearance of a characteristic color, which can be easily distinguished from the color of a control test in which boric acid is absent.

The results obtained are given below.

Formula of Reagent	Color of the dry residue		Sensitivity of the reaction for boric acid	
	without boric acid	with boric acid	limit of identification	limiting conc.
	Greyish-yellow	Reddish-brown	100	1:500
	Yellowish-brown	Brick-red	2.5	1:20000
	Yellow	Violet	2.5	1:20000
 Hematoxylene	Yellow	Ditto	2.5	1:20000

Formula of Reagent	Color with Boric Acid	Limiting Conc.
	Orange	1:500
	Violet	1:20000
	Orange-yellow	1:100
	Brick-red	1:20000

We compared some of these reagents with analogous derivatives of salicylic acid [1].

It is clear that the pyrocatechol derivatives give more intense colors with boric acid than the corresponding derivatives of salicylic acid. The reactions for the pyrocatechol derivatives are also more sensitive.

SUMMARY

1. It has been shown that organic compounds which give five membered inner complex rings with boron, can be used as reagents for boric acid. It was first experimentally shown that removal of one of the carbon atoms from a six membered ring does not radically change the analytical properties of the compound.

2. It has been shown that some azodyes – derivatives of pyrocatechol and of hematoxylene, which is itself a derivative of pyrocatechol – are capable of giving fairly sensitive, color reactions with boric acid.

Received March 30, 1948

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CRITICISM AND BIBLIOGRAPHY

Yu. V. Karyakin. "Acid-Base Indicators". Theoretical Bases and Practical Application. State Chem. Press. 1951, 198 pp, 11 roubles 65 kopecks.

The appearance of this book is very timely. Up to now only a translation of Kolthoff's book "Application of Colored Indicators" (1929) has been available in the Russian language, and the subject matter in this book is very much dated. Karyakin's book, which is smaller, contains more new facts on the theory of acid-base indicators, their properties and applications. The book consists of an Introduction and seven chapters. In the Introduction the author analyzes the advantages and disadvantages of the colorimetric method for the determination of hydrogen ion concentration, he regards the limiting accuracy of the method as 0.01 pH units. Such an accuracy is scarcely ever attainable by visual determination of pH without the help of some apparatus. In Chapter I "The concept of the acidity of a solution", it should have been shown (page 9) that at room temperature $pH + pOH = 14$, since this relation enables pOH to be rapidly determined from the value of pH. It would have been useful to indicate that pH can have negative values and be greater than 14. In Chapter II the author in a concise manner deals with the behavior of electrolytes in aqueous solutions. On p. 23 in discussing the properties of buffer solutions, it should have been said that the pH of such solutions changes very little on dilution. In the same chapter in the section of "Preparation of buffer solutions", considerably more information should have been given, including information on the large number of buffer mixtures of vital practical importance. The method of making up mixture 2 contains a very serious error.

V should refer not to the solution of biphthalate but to hydrochloric acid. There are a number of smaller errors. Thus in buffer mixture 4, for a pH 6.4 - V should be 12.6 ml and at a pH 6.8 should be 23.65 ml. For the preparation of buffer mixture 12, solutions 0.4 M with respect to H_3PO_4, 0.04 N with respect to CH_3COOH and 0.04 M with respect to H_3BO_3 should be used and not equal volumes of the three solutions. In the discussion on the purification of chemicals used for the preparation of buffers, the author says nothing about the use of chemically pure reagents with respective GOST[1] numbers, e.g. Potassium biphthalate with a Gost number - GOST 5858-51 but confines himself to indicating the methods for the purification of "bought chemicals", which in the majority of cases is hardly profitable. Nothing is said about the use of hygrostats (e.g. for borax). The preparation of strong alkali solutions involving the use of ether and metallic sodium should not be recommended because of the inflammability of the ether.

The literature on this section of the book is very meagre. There is no reference to R. I. Alekseev's article in the book "Reagents and Preparations for Laboratory Purposes" under V. V. Loginov's editorship, where there is information on buffer mixtures published in the literature.

In Chapter III the author briefly discusses the theory of acid-base indicators. This chapter states the contemporary state of the question. It is unfortunate that the mathematical interpretation of these theories is relegated to the next chapter by the author.

In Chapter IV "The transition interval" the author discusses the behavior of indicators in solutions quantitatively. A table is included which gives the pH intervals for color changes for a large number of indicators.

1) GOST = All-Union State Standard.

It is well known that there are a number of contradictions in the literature on this subject. It is necessary therefore to point out the literature references in separate cases, from which the respective data has been compiled; this has not been done in the book under review. All the current indicators most widely used are included in GOST 4919-49, in which pH intervals are also given. These GOST results should have been indicated, but the author does not even mention GOST. In some cases it is not clear which indicators are under discussion, because the structure is not given. E.g. in addition to the normal methyl red, other methyl reds with different pH intervals are given (p.69). The concept of pK as the pH at which 50% of the indicator is in the alkaline form and the other 50% in the acid form, should have been given on p.65 and not on p.84, since it should logically precede the table mentioned above. Fluorescent indicators are recommended (see Table on p.106) without a sufficiently critical evaluation of their properties. For β-methylumbelliferone the pH interval is given as 6-7.2, while according to Pukirev and Maslova (Factory Lab. 11, 1038, 1934) max. fluorescence corresponds to a pH of 7.2-7.4. To call ultraviolet radiation "black light" (p.107) does not follow. The section on "sensitivity of indicators" has been compiled in rather an abstract manner. The sensitivity of an indicator can be defined in the same manner as for other reagents for color reactions. (see P. I. Alekseev's article, loc.cit.). The absence of a chapter on the "Testing of Indicators" is a serious omission.

In Chapter V the author considers the question of pH change during titration, but does not say anything re the fact that curves which express the relation between pH and the number of mls of added acid or alkali can be obtained either by calculation or potentiometrically. In this connection the derivation of pT is somewhat nebulously expressed; at this juncture something should have been said about titration with "observers". In speaking of the increase in accuracy of titration it would have been useful to mention the application of "macro-micro burettes" (See Factory Lab.7, 627, 1938). On p.126, green is called the supplementary color to violet.

In Chapter VI colorimetric methods for the determination of pH are considered and the effect of salts, organic solvents and other materials discussed.

This chapter is well put together - the section on the mistakes which can arise in the determination of pH contains many new results. The comparator should have been mentioned in this chapter when discussing the determination of pH without buffers (p.134). This simple apparatus is described in the next chapter on p.170. In the section on universal indicators (p.139) it is completely useless to give the composition of these indicators without giving the respective amounts of each component.

For the universal indicator "MVF" (p.141) there is no indication of the pH range. It should have been pointed out that when working with universal indicators it is possible to use a color scale made on paper.

In Chapter VII "The colorimetric determination of pH in turbid and colored solutions" new data are presented. The author's own results are included for the determination of pH with organic solvents which do not mix with the solutions whose pH is being determined but which extract the indicator to different extents.

A very useful set of indicators recommended by the author for specific purposes is included. Literature relating to different sections of the book is distributed throughout the book rather unsuccessfully. There is no reference to Kolthoff and Laitinen's book "Determination of Hydrogen Ion Concentration and Electrotitration", Moscow 1947. Without dealing with smaller drawbacks in this book we should like to say that Yu. V. Karyakin's book despite a number of drawbacks is a valuable textbook for workers in Scientific-Research Laboratories.

G. A. Pevtsov

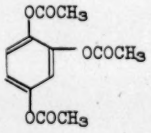
NEW REAGENTS

"PYROGALLOL A"

A chemical reagent for the determination of oxygen in gas analysis. (Catalog of chemical reagents and preparations. Bureau of Chemical Reagents, State Chemical Press, 1951, No. 1907.

A new chemical reagent for the determination of oxygen in gas analyses, "Pyrogallol A" has been proposed by the Institute of Chemical Reagents.

"Pyrogallol A" is hydroxyhydroquinone triacetate (1,2,4-trihydroxybenzene triacetate)



1 mole of "Pyrogallol A" absorbs an equal amount of oxygen, 1.5 mole, ordinary pyrogallol (1,2,3-trihydroxybenzene).

The advantage of "Pyrogallol A" as compared with ordinary pyrogallol is that on absorption of oxygen it does not evolve CO.

"Pyrogallol A" is a valuable substitute for ordin ry pyrogallol in the determination of oxygen in gas analysis.

"Pyrogallol A" is on sale at all the shops of the Bureau of Chemical Reagents. Instructions for the use of "Pyrogallol A" for the determination of oxygen in gas analysis is enclosed with each packet of reagent.

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A COMPARISON OF THE CHARACTERISTICS OF CERTAIN ION EXCHANGE RESINS

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(The V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R Academy of Sciences, Moscow)

Tsvet's chromatographic method [1] is widely used at the present time both in scientific research and in a number of branches of industry [2-4]. It is of particular importance in analytical chemistry [5-10]. We may mention, e.g. [8,9], the chromatographic separation of aluminum from zinc and iron, of arsenic from tin and antimony, the separation of metals in the presence of complex-forming compounds (separation of bismuth from copper and lead, and of tin from antimony), the determination of small amounts of sulfur, phosphorus and arsenic in nickel and copper. The determination of molybdenum in ferro-molybdenum with the help of sulfonated coal is of great interest [10]. The chromatographic determination of copper and iron in ceramic melts is of great importance.

Illustrative of the importance of the chromatographic method for analytical chemists is the extraordinary interest which the report read by V. N. Lenska on chromatography at the Conference on Classical Methods of Chemical Analysis[1] evoked.

The simplest problems of chromatographic analysis (e.g. the separation of components in the anionic form from a mixture of cations) can be solved in practice by means of any ion exchange material. But more complicated problems (e.g., separation of a mixture of cations which possess similar properties,etc.), can only be solved by the correct choice of all the experimental variables, particularly of the ion-exchange resin.

During the post-war years a number of institutes and enterprises in our country have achieved considerable success in the production of high-quality ion-exchange resins. Nevertheless as was demonstrated at the conference mentioned above, the overwhelming majority of analytical chemists are totally unacquainted with the brands of ion-exchange resins available and their characteristics. The present article is an attempt to fill the gap to some extent, and to acquaint a wide circle of analysts with the fundamental properties of cationites and anionites[2] at our disposal in comparison with foreign brands.

Synthetic resins used for ionic exchange purposes in their structure and

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[1] The conference was held on the 14-17th of November, 1951, in Moscow.

[2] In our work factory produced ion-exchange resins were used as well as those developed and prepared in the Mendeleev MKhTI. The authors wish to express their gratitude to I. P. Losev and A. B. Davankov for a gift of samples and for their close cooperation in the work. (MKhTI = Moscow Chem.-Tech. Inst.).

chemical composition are very similar to those synthetic resins used industrially as plastics, and are obtained in a similar fashion by condensation and polymerization [11]. According to our result on the elemental analysis of ion exchange resins of foreign manufacture the American cationite Amberlite IR-120 is prepared by polymerization, while the German Wofatit is a condensation product of phenol and formaldehyde. Preference should be given to polymerization ion exchange resins because of their greater chemical stability and because of the possibility of preparing unifunctional cationites by polymerization.

There are a number of requirements for resins used for the preparation of plastics and ion exchange purposes which are identical. Firstly a high mechanical stability, insolubility in water and the usual organic solvents, and low tendency to swell. Mechanical stability and insolubility can be attained by a high degree of condensation or polymerization and by the formation of a net-like three-dimensional structure for the polymer.

In the production of resins to be used as plastics, all technological processes are directed to making a chemically inactive product. In the production of ion exchange resins on the other hand it is endeavored to give them a more active character.

In accordance with their chemical nature all synthetic exchange resins used in practice for ion exchange can be divided into two groups. The first group comprises those resins which have acidic properties and can be used for the exchange of cations- cationites. While to the second group belong those resins which have basic properties and can be used for the exchange of anions - anionites. Cationites usually contain the active groups: $-SO_3H$; $-CH_2SO_3H$; $-COOH$, phenolic groups $-OH$, etc. The ion-exchange properties of anionites are determined by the presence of amine and imine groups.

The processes of exchange and regeneration of ion-exchange resins are described by the following reactions:

$$\text{Cationite: } 3RNa + FeCl_3 \rightleftarrows R_3Fe + 3NaCl \text{ (exchange)}$$
$$RNa + HCl \rightleftarrows RH + NaCl \text{ (regeneration)}$$

$$\text{Anionite: } 2RCl + H_2SO_4 \rightleftarrows R_2SO_4 + HCl \text{ (exchange)}$$
$$RCl + NaOH \rightleftarrows ROH + NaCl \text{ (regeneration)}$$

Before considering the characteristic properties of ion-exchange resins, which depend on their nature, we should like to point out the desirable features of ion-exchange resins from the point of view of chromatographic analysis.

In the production of ion-exchange resins, particles of both spherical forms and other forms not so desirable may be prepared. From the standpoint of chromatographic analysis there is no doubt that spherical particles are the most desirable, since they ensure close and even packing of the ion-exchange resin in a column, which in turn leads to a fuller use of the exchange capacity as a result of the favorable hydrodynamical conditions. The extent to which the ion-exchange resin will be used will also be greater the closer to equilibrium the operating conditions of the column.

The kinetics of the ion-exchange process in the overwhelming majority of cases is determined by the diffusion of the ions to the grain surfaces and inside them. The smaller the grain size, the faster is the equilibrium distribution of the ions between solution and the ion-exchange resin achieved, i.e. the faster the exchange process. In this connection the resistance of the layer is a limiting factor, which increases with decreasing grain size.

It is sometimes stated that a decrease in grain size leads to an increase in the static exchange capacity. This is incorrect, since ion-exchange resins have

a porous structure. As proof of the porosity of ion-exchange resins we quote the experimental results in Table 1 where it is shown that the static capacity of one of the Wofatit samples is independent of the grain size. It is obvious that the increase in the external surface as a result of grinding of the grains is practically negligible in comparison with the total surface of the porous ion-exchange resin.

Of the properties which depend on the nature of the ion-exchange resin, we have considered in the present article:, specific gravity, extent of swelling, static exchange capacity, and the potentiometric titration curves of the ion-exchange resins.

TABLE 1

Grain size in mm	Static exchange capacity in mg-equiv./g
<0.2	2.78
0.2 - 0.35	2.78
0.5 - 0.75	2.79
0.75 - 1.0	2.74
1.0 - 1.5	2.69

A knowledge of these fundamental characteristics will enable a rational choice to be made of ion-exchange resins for some of the actual problems which confront analytical chemists.

Before starting to test these samples they were all treated in accordance with the testing methods for ion-exchange resins for confirmation of their quality according to All-Union State Standard (5695-52).

Cationites were purified from mineral contaminants and converted into the hydrogen form by treating them with 2N HCl, followed by washing with distilled water till no reaction for chloride is given. Anionites were treated, first with 2 N HCl as for the cationites, and then for conversion into the hydroxyl form with 4% NaOH solution, followed by washing free from excess alkali with distilled water.

It should be noted that it is sometimes recommended that anionites may be converted into the hydroxyl form by treatment with 5% sodium bicarbonate (pH~8). If such a treatment is given, strongly basic anionites may be converted into the bicarbonate form, and as our experimental results show (see Fig.6) even weakly basic anionites are not completely converted into the hydroxyl form by the bicarbonate.

All tests were conducted with air-dried ion-exchange resins.

It is necessary to pay special attention to the removal of mineral contamination from ion-exchange resins. According to GOST[1] a solution of potassium thiocyanate may be used for checking the removal of mineral contaminants, since iron is the most likely contaminant as the result of the use of apparatus made of that metal for manufacturing the resins. In conducting an analysis of a definite mixture of elements it must be checked beforehand that these elements are absent in the resin to be used. In addition, it should be borne in mind that the resin might contain some of the original unreacted organic components, which might possess reducing properties. In some cases, where the chemical stability of the resin is insufficient, some of the organic material might be transferred into the filtrate.

The Physical Properties of Ion-Exchange Resins

According to GOST methods of testing ion-exchange resins, the following physical-mechanical properties are determined: moisture content, specific gravity (of the granular dry material, i.e. the apparent specific gravity), extent of swelling in water, mechanical stability, and granular composition.

The moisture content of an ion-exchange resin, which depends on the relative humidity of the air, is not of fundamental importance for the analytical applications of cationites or anionites, so that no figures on the moisture content are

1) GOST = All-Union State Standard.

given in the present paper. Mechanical stability, while important for industrial applications of ion-exchange resins, is of no interest for analytical chemists.

The granular composition of an ion-exchange resin produced industrially is not important in the application of ion-exchange resins for analytical purposes, since according to what has been said above very small grains should be chosen. Thus for technical purposes, grains of Espatite-1 whose diameter is less than 0.3 mm are regarded as waste products; at the same time fractions less than 0.1-0.2 mm are quite often used. In the present article therefore only results on the apparent specific gravity and the relative extent of swelling are given. These determinations were made according to GOST in measuring cylinders with samples of ca.10 g. Since ion-exchange resins are used in other solvents as well as water for analytical purposes, results for extent of swelling are given in water, N KCl, benzene and butyl alcohol.

The true specific gravity of an ion-exchange resin was determined as follows. A known weight of the resin was placed in a weighed pycnometer. The resin was covered with benzene and the pycnometer reweighed. The difference in weights gives the weight of benzene. The volume of benzene was determined from its specific gravity at the temperature of the experiment. From the difference in volume of the pycnometer and the benzene the volume of the resin was determined. By dividing the weight of ion-exchange resin by its volume the true specific gravity was determined.

It is natural that the degree of separation attained in a chromatographic experiment is greater, the greater the exchange capacity of the resin in the column. For a given static capacity of an unit weight of an ion-exchange resin, the exchange capacity of the resin in the column is greater, the greater the apparent specific gravity of the resin and the smaller its relative extent of swelling.

A knowledge of this latter quality is also of great importance, because the capacity of an ion-exchange resin (in the absence of complex forming compounds) is higher, the lower its extent of swelling, since in this case separation is connected with hydration of the ions [12]; in the case of a strongly swollen ion-exchange resin, ions of different degrees of hydration will be adsorbed by the resin to practically the same extent; on the other hand, in the case of a polymer with a stable structure only the non-hydrated ions will be sorbed, and differences in the energy of hydration will lead to a separation of the mixture being analyzed into its components.

Experimental results on the specific gravity and relative degree of swelling of the cationites examined are given in Table 2.

On the basis of these results the following conclusions can be drawn:

1. The degree of swelling depends essentially on the nature of the solvent. Maximum swelling occurs in non-polar solvents such as benzene. On the other hand the swelling in butyl alcohol is particularly high.

2. The ion-exchange resins SDV-1, SDV-2, KN, KM, Dowex-50 and Amberlite IR-120 swell less in N KCl than in water; Espatite-1, SBS, Amberlite IRC-50 and Wofatit P and C swell more in KCl than in water. Swelling of sulfonated coal in water and N KCl is the same. Naturally the increase in volume of an ion-exchange resin in a solution of KCl depends not only on the swelling in the medium but also on the partial conversion of the cationite into the potassium form.

3. For separating mixtures in the absence of complex-forming compounds the most suitable resin, according to it relative degree of swelling, is SBS.

TABLE 2

Designation	Relative degree of swelling, %				Specific gravity	
	Water	1N KCl	Benzene	Butyl alcohol	Apparent	True
Espatite-1	14	50	0	62	0.74	1.33
SBS	0	14	8	34	0.57	1.29
SDV-1	190	119	–	–	0.65	–
SDV-2	135	70	–	–	0.50	–
KN	25	22	–	–	0.40	–
KM	108	85	–	–	0.48	–
Sulfonated coal	33	33	–	–	0.67	–
Dowex-50	24	16	0	15	0.80	1.32
Amberlite IR-120	26	18	0	17	0.71	1.29
Amberlite IRC-50	36	62	4	62	0.70	1.31
Wofatit P	12	17	4	30	0.69	1.31
Wofatit C	12	41	4	40	0.83	1.35

4. The apparent specific gravity of the cationites lies within the range 0.40-0.83 g/cm^3. The low apparent specific gravities of SBS and KN are to some extent compensated by their relative degrees of swelling.

5. The true specific gravity is practically the same for all the cationites.

Results for the physical properties of anionites are given in Table 3.

TABLE 3

Designation	Relative degree of swelling, %			Specific gravity	
	Water	1N KCl	Benzene	Apparent	True
MN	40	25	–	0.63	–
TN	1	6	–	0.34	–
N-0	23	29	–	0.25	–
MMG-1	24	23	0	0.80	1.433
N	21	18	5	0.52	1.410
VS	27	16	0	0.34	1.546
TM	12	15	4	0.80	1.492
Wofatit E	44	31	–	0.80	1.485
Wofatit M	26	25	5	0.76	1.447
Amberlite IR-4B	41	33	0	0.64	1.276
Amberlite IRA-400	41	31	6	0.68	1.194

From Table 3 it can be seen that the swelling of a given anionite in water and 1 N KCl is almost identical. In a non-polar solvent such as benzene, anionites show minimum swelling. Anionites can be divided into three groups according to their swelling capacity:

a) anionites with a small degree of swelling, up to 21% (TN, N, TM);

b) anionites with average degrees of swelling (MMG-1, VS, N-0, Wofatit M);

c) anionites with large degrees of swelling, 40% (MK, Wolfatit-E, Amberlites IR-4B and IRA-400).

The small apparent specific gravities of anionites N-0, VS and TN are worthy of note.

From the tables it can be seen that the true specific gravity is practically the same for all the anionites with the exception of Amberlite IR-4B and IRA-400 which are characterized by a comparatively small value for the true specific gravity. The true specific gravity of VS is relatively high while its apparent specific gravity is very small, which possibly testifies to the large porosity of this resin.

Exchange Properties

The most important characteristic of an ion-exchange material is its exchange capacity, which is determined by the number of functional groups containing ions which can be exchanged. The exchange capacity of a resin is usually characterized by the values of the Total Exchange Capacity (TEC), the Static Exchange Capacity (SEC), the Dynamic Capacity at the point where ions stream through (DEC), and the Dynamic Exchange Capacity at the point where the concentration in the layer reaches its initial value (IDEC).

Both the Total and Static Exchange Capacities are determined under static conditions. The essential difference between these two capacities is that the Total Exchange Capacity gives the exchange capacity for any exactly known pH value of the equilibrium solution, while the Static Exchange Capacity characterizes the capacity for unknown pH's, which depend on the nature of the ion-exchange resin and the exchange ion, and also on the amount of ion-exchange resin and the concentration of the solution. The uncertainty in the pH value of the equilibrium solution in the determination of the Static Exchange Capacity is the consequence of the fact that the concentration of the hydrogen ions is equivalent to the number of the adsorbing ion exchange cations or anions, i.e. its capacity for a given set of experimental conditions. When this fact is taken into consideration, it becomes comprehensible that the Static Exchange Capacity has a physical significance only when it is determined under conditions for which the pH of the original and equilibrium solutions do not differ too much from each other (in excess alkali or acid).

The value of the Dynamic Exchange Capacity up to the point at which ions pass through the column (DEC) is determined by both static and kinetic factors and accordingly depends essentially not only on the nature of the ion exchange resin but also on grain size, flow speed of the solution, etc. A knowledge of this value is important for the calculation of set ups for softening and demineralizing water, for decolorizing solutions, extraction of valuable materials from waste products, etc. and is of no less importance for chromatographic analysis. The value of IDEC is identical with one of the values of the Total Exchange Capacity for a corresponding acidity of the solution.

In accordance with the concepts postulated above, results are given for the Static Exchange Capacity of cationites and anionites (determined both in acid and alkalies). Curves which express the Total Exchange Capacity at different pH values of the equilibrium solution are also given [13-14].

The Static Exchange Capacity was determined for 0.1N NaOH (for cationites) and 0.1N HCl (for anionites) by keeping a known weight of the ion-exchange resin in an excess of the acid or alkaline solution and titrating the non-reacted reagent with phenol red as indicator after filtering off the resin. The Total Exchange Capacity was determined according to GOST by potentiometric titration. The respective results are given in Tables 4 and 5 and in Figs. 1-10.

From Table 4 it can be seen that SDV-1, Amberlite IR-120, Dowex-50 have a very high capacity; the capacity of the remaining cationites, which is determined by the sulfonate group, is not greater than 4 mg-equiv./g.

TABLE 4

Cationite	Static Exchange Capacity
Espatite-1	4.4
SBS	3.5
SDV-1	4.3
SDV-2	4.0
KN	2.8
KM	9.4
Sulfonated coal	3.6
Dowex-50	4.9
Amberlite IR-120	4.7
Amberlite IRC-50	9.2
Wofatit P	3.9
Wofatit C	6.4

TABLE 5

Anionite	Static Exchange Capacity
MN	4.1
TN	3.2
NO	3.9
MMG-1	4.2
N	4.4
VS	3.4
TM	4.0
Wofatit E	3.4
Wofatit M	3.2
Amberlite IR-4B	8.0
Amberlite IRA-400	1.6

Cationites containing carboxyl functional groups (KM, Amberlite IRC-50 and Wofatit C) have the greatest exchange capacity. The high capacity of carboxyl ion-exchange resins testifies to the fact that in the method used for their preparation it is possible to introduce several carboxyl groups into one benzene ring. As Ryabchikov showed [15-16], numerous carboxylic acids form stable complex compounds, e.g. with the rare earths; as a result of this the cationites mentioned above can exhibit a selective action in relation to a number of elements.

This comparatively high exchange capacity of carboxyl cationite, however, is only manifested in alkaline media. As a result of the high degree of dissociation of the sulfonic acid, its hydrogen ions can be substituted by metals even in very acid solution; since the carboxylic acids are comparatively weak, their exchange capacity in acid solution will be practically zero, as graphically shown by the potentiometric titration curves.

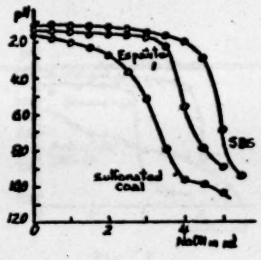

Fig. 1

From Table 5 it can be seen that the anionites MMG-1, N, TM and Amberlite IR-4B have a comparatively large capacity.

It is interesting to note that in contrast to cationites which contain sulfonate groups, the experimentally determined exchange capacity for anionites, with the exception of Amberlite IR-4B, is considerably lower than the capacity calculated from the percentage of nitrogen.

The potentiometric titration curves for cationites (Figs.1-4) can be divided into three groups according to their shape.

1) The curves derived by titration of the cationites SDV-1, SDV-2, SBS, Dowex-50 and Amberlite IR-120. These curves are similar to those of strong acids. Therefore it can be postulated that these brands of cationites contain only sulfonate groups on the benzene ring.

2) The titration curves of KN, KM, Amberlite IRC-50 and Wofatit C. These curves are similar to those for titration curves of comparatively weak acids. The step-wise character of the titration curves of KM and Amberlite IRC-50,

which is worthy of attention, is possibly explained by the presence of multibasic highly polymerized acids. The hypotheses that a few carboxyl groups enter into the benzene ring of the ion-exchange resin is confirmed by their very high Static Capacity (9.4, 9.2 mg-equiv/g).

3) Titration curves of Espatite-1, sulfonated coal, and Wofatit-P are intermediate between those of the first and second groups; on the one hand they have a fairly clearly defined horizontal part while on the other hand there is an even slope of the curve on addition of sufficient alkali. This may be explained by the presence of two types of acid groups in the cationites of the brands indicated (sulfonate and carboxyl or hydroxyl groups), or by the presence of sulfonate groups in the side chain.

For chromatographic analyses the most suitable cationites are those which possess maximum capacity at the pH of the solution being analyzed. It is appropriate to note that experiments can be carried out qualitatively only by bringing the ion-exchange resin into equilibrium with the washing solution beforehand. Values for the Total Exchange Capacity of the cationites for 3 pH values calculated from the potentiometric titration curves are given in Table 6.

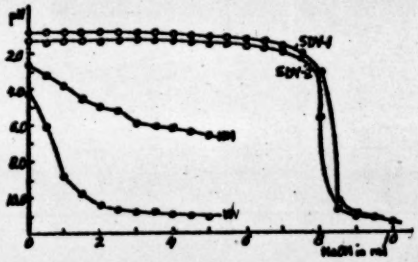

Fig. 2

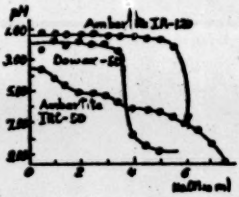

Fig. 3

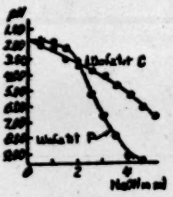

Fig. 4

Cationites the capacity of which does not depend on the acidity of the solution are sometimes called universal cationites.

The definite increase in capacity of a number of cationites on increasing the pH made it expedient to carry out experiments on less acid media. In chromatographic analysis in which complex-forming substances are used, this can be achieved by a corresponding decrease in the concentration of the complex-forming compounds. In view of the existing relation between the instability coefficients

of the complexes and the acidity of the solution, and its independence of the concentration of the components, the same relation between the normal and complex forms can exist in media of different acidities for a corresponding change in the concentration of complex-forming compounds.

TABLE 6

Cationite	pH		
	3	5	7
Espatite-1	1.9	2.0	2.1
SBS	2.25	2.4	2.5
SDV-1	4.0	4.2	4.3
KM	0.15	1.0	2.7
Sulfonated coals	1.0	1.5	1.7

On the basis of the potentiometric titrations of the anionites (Figs.5-10) the following conclusions can be drawn.

1) All the anionites tested can be divided into 2 groups (for a pH of 7).

2) Anionites of the first group can be used in neutral and even weakly alkaline media, while anionites belonging to the second and third group (weakly basic anionites) can only be used in acid media.

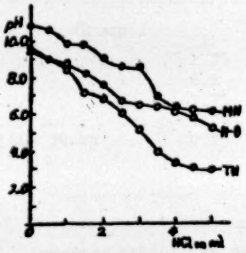

Fig. 5

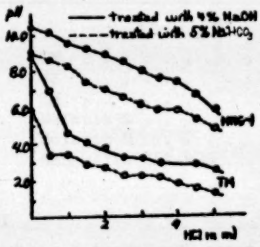

Fig. 6

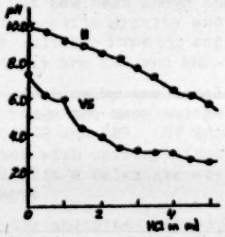

Fig. 7

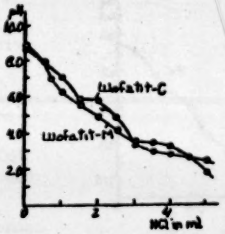

Fig. 8

3) From a comparison of the potentiometric titrations of anionites to convert them into the hydroxyl form with both 5% $NaHCO_3$ and 4% NaOH (see Fig.6) it is possible to conclude that even the weakly basic anionites are not completely converted into the hydroxyl form by means of 5% $NaHCO_3$.

4) From the shape of the potentiometric titration curves for VS, given a preliminary treatment with HCl (Fig.10), it can be postulated that this resin is amphoteric, i.e. possesses cationite properties as well. However this conclusion, based only on potentiometric titration, is not sufficiently reliable,

since curves of a similar type can be derived for anionites with weakly basic functional groups.

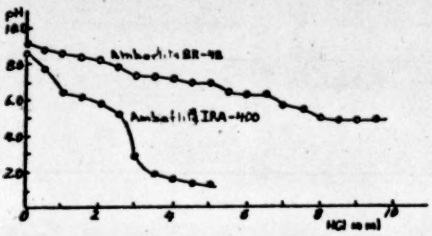

Fig. 9

Group I		Group II	
NO	1.25	TN	0.75
MMG-1	2.2	VS	0.2
N	1.75	TM	0.25
MN	1.75	Wofatit E	0.5
Amberlite IR-4B	2.15	Wofatit M	0.4
		Amberlite IRA-400	0.4

SUMMARY

1. Domestic cationites and anionites have been tested and compared with the best foreign ion-exchange resins from the point of view of their use in chemical analysis.

2. It has been shown that according to the apparent specific gravity and degree of swelling, the most suitable domestic cationite and anionite respectively are SBS and MMG-1.

3. Judging by the total capacity within a wide pH range the most suitable cationites are SDV-1, SDV-2 and SBS. Of interest are those cationites with carboxyl functional groups (KM), which exhibit a selective action toward a number of elements.

Of the anionites tested, MMG-1 is recommended for analytical purposes

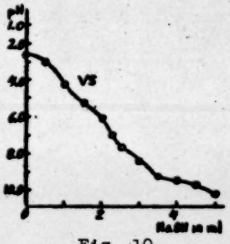

Fig. 10

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TITRATION OF MIXTURES OF TWO ACIDS OR THEIR SALTS

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The titration of mixtures of two acids has been treated in an elementary form by Noyes [1] and his conclusions were used by Kolthoff [2]. A detailed examination of the question from the standpoint of potentiometric analysis was given by Roller [3]. In this paper the same question is considered from the viewpoint of ionic equilibrium, but individual problems are solved in a general form, and simplifications introduced only in the order of the analysis of the general solution.

Let us assume that to a mixture of two weak acids HA_1 and HA_2 there is added an amount of NaOH solution such that the initial concentrations of the three components are equal: $c_{HA_1} = c_1$ and $c_{HA_2} = c_2$ and $c_{NaOH} = c_1$ mols/liter. Such a system corresponds to the first stoichiometric point. If we assume that at the moment when all HA_1 is completely neutralized HA_2 is completely untouched, then the initial conditions can be represented by the following scheme:

$$c_{A_1^-} = c_1,\ c_{HA_2} = c_2,\ c_{Na^+} = c_1.$$

It is obvious that the equilibrium in this system will be determined by the equations:

$$HA_2 \rightleftarrows H^+ + A_2^-; \quad H^+ + A_1^- \rightleftarrows HA_1.$$

This system contains 5 unknowns: $[H^+] = x$; $[A_1^-] = y$; $[A_2^-] = z$; $[HA_1] = u$, $[HA_2] = t$ and $[Na^+] = c_1$, in which the formula in the square brackets both here and in the rest of this paper denote the equilibrium concentrations. It is obvious that for the calculation of the equilibrium the following equations can be used:

$$xy = k_1 u;$$

$$xz = k_2 t;$$

$$c_1 = y + u;$$

$$c_2 = z + t;$$

$$c_1 + x = y + z.$$

This system of equations can be easily transformed into a cubic equation in x:

$$x^3 + (c_1 + k_1 + k_2)x^2 + (k_1k_2 + k_2c_1 - k_2c_2)x - k_1k_2c_2 = 0. \qquad (1)$$

By means of this equation it is possible to calculate $[H^+]$ and pH for the first stoichiometric point, i.e., at the moment when an amount of NaOH has been added to the mixture of acids which is equivalent to the initial concentration HA_1.

Equation (1) reduces to the formulas of Noyes and Kolthoff when the following simplifications are introduced:

1) for $c_1 = c_2 = c$ the equation can be rewritten in the form

$$(x + c + k_1 + k_2)x^2 - k_1k_2(c - x) = 0;$$

2) for $x \ll c$

$$x = [H^+] = \sqrt{\frac{k_1k_2c}{c + k_1 + k_2}};$$

3) for $k_2 \ll k_1$ and $\underline{c}$ we get Noyes' formula, which Kolthoff regards as exact, while for $k_1 \ll c$ we get the simplified formula of Kolthoff. It is obvious that the first assumption is automatically satisfied during the titration of weak dibasic acids, but is inadmissible for theoretical investigations of the titration of mixtures of two weak acids, if the conditions $c_1 = c_2$ remain unfulfilled.

For an exact calculation of pH in those cases where the initial concentration of NaOH in the system satisfies the condition $c_1 < c_{NaOH} = c < c_1 + c_2$ it is possible to use the equation

$$x^3 + (c + k_1 + k_2)x^2 + [(c - c_1)k_1 + (c - c_2)k_2 + k_1k_2]x - \\ - k_1k_2[c_2 - (c - c_1)] = 0. \qquad (2)$$

It can be derived exactly the same as (1) and can be converted into the latter when $c = c_1$. If $x = [H^+] \ll c$ then Equation (2) transforms into the quadratic equation:

$$(c + k_1 + k_2)x_2 + [(c - c_1)k_1 + (c - c_2)k_2 + k_1k_2]x - k_1k_2[c_2 - (c - c_1)] = 0.$$

The solution of the quantitative determination of one weak acid HA_1 in the presence of another HA_2 is connected with the problem of the distribution of the alkali between two acids. If $c_{HA_1} = c_1$, $c_{HA_2} = c_2$, and the system contains $c_{NaOH} = c_1$, then it can always be postulated that αc_1 mol of NaOH has been used for the neutralization of HA_1 and yields αc_1 mols of A_1^- ions. Then, it follows that $(1 - \alpha)c_1$ mol. of NaOH has been used for neutralizing HA_2, which means that $(1 - \alpha)c_1$ mols of A_2^- ions should be formed. In such a case it is possible to regard the equilibrium concentration of the OH^- ions to be vanishingly small, since the system contains free acid. Under these conditions the equilibrium concentrations are expressed as follows:

$[A_1^-] = \alpha c_1$, $[HA_1] = c_1(1 - \alpha)$, $[A_2^-] = (1 - \alpha)\cdot c_1$, $[HA_2] = c_2 - (1 - \alpha)c_1$ and

$$[H^+] = h.$$

If, further $k_{HA_1} = k_1$ and $k_{HA_2} = k_2$, then obviously:

$$h\alpha c_1 = k_1c_1\ (1 - \alpha)$$

and

$$hc_1(1 - \alpha) = k_2[c_2 - (1 - \alpha)c_1].$$

After dividing one equation by the other and transposing we find that

$$\frac{k_1}{k_2} = \frac{\alpha}{(1 - \alpha)^2}\left[\frac{c_2}{c_1} - (1 - \alpha)\right]. \qquad (3)$$

This expression shows that the possibility of determining one weak acid in the presence of another depends not only on the ratio of their dissociation constants, as Kolthoff showed but also on the ratio of their initial concentrations. Formula (3) completely charscterizes the possibility of titrating two weak acids in aqueous solution with a fixed degree of accuracy. If, for a given value of α and the expected ratio of the initial concentrations, c_2/c_1, the actual ratio of the constants is less than the limiting value, then the separate determination of the acids in aqueous solution is impossible. In similar cases the problem could be solved by the application of differential solvents [6,7].

Consideration of the distribution of alkali between two weak acids in a general way can also enable a number of important conclusions to be drawn. Let us take 1 liter of solution containing c_1 mols of HA_1 and c_2 mols of HA_2 and to it add $\underline{v}$ liters of a c-molar solution of NaOH. Let $k_{HA_1} = k_1$, $k_{HA_2} = k_2$, $k_1 > k_2$, and $c_1 < cv < c_1 + c_2$. In this case it can be accepted that $c_{HA_1} = \frac{c_1}{1 + v}$, $c_{HA_2} = \frac{c_2}{1 + v}$ and $c_{Na^+} = c_{OH} = \frac{cv}{1 + v}$. Assume that for the neutralization

of HA_1 an α part of the NaOH was used, then applying the above considerations we get the equations:

$$\frac{h\alpha cv}{1+v} = \frac{k_1(c_1 - \alpha cv)}{1+v} \tag{4}$$

and

$$\frac{h(1-\alpha)cv}{1+v} = \frac{k_2[c_2 - (1-\alpha)cv]}{1+v} \tag{5}$$

The product cv, which enters both equations, is equal to the number of mols of NaOH which was added to 1 liter of the mixture, containing c_1 mols of acid HA_1 and c_2 mols of acid HA_2 in order to get a pH corresponding to $[H^+] = h$, which enter into Equations (4) and (5). Let cv be denoted by z, then solving the system with respect to z and α, we get:

$$\alpha = \frac{c_1k_1(h+k_2)}{c_1k_1(h+k_2) + k_2c_2(h+k_1)} \tag{6}$$

and

$$z = cv = \frac{k_2}{h+k_2}\,c_2 + \frac{k_1}{h+k_1}\,c_1. \tag{7}$$

With the help of Formula (6) it is possible to calculate the distribution of alkali between the two weak acids, if $c_1 < cv < c_1 + c_2$. Formula (7) is far more important. It shows that the number of mols of NaOH expended on attaining any given pH lies between the first and second stoichiometric points and is a linear function of the initial concentrations of the weak acids c_1 and c_2. But if this is so, then by titrating the same mixture to different pH values and noting the respective values of h_i and z_i where i is the number of the respective value, it is possible to find the required values of c_1 and c_2, i.e., to determine the required concentrations of both the weak acids.

Finally, using Formula (6) it is possible to find in a general form the indicator error of the titration. It is obvious that this error is equal to $cv - c_1$, if $c_{HA_1} = c_1$ and if the titration is interrupted when the hydrogen ion concentration H^+ attains the value h. After substitution and simplification we find that the absolute indicator error will be equal to

$$cv - c_1 = z - c_1 = \frac{c_2k_2}{h+k_2} - \frac{hc_1}{h+k_1}, \tag{8}$$

and the relative error given by

$$\frac{z - c_1}{c_1} \cdot 100 = \frac{k_2}{h+k_2} \cdot \frac{c_2}{c_1} - \frac{h}{h+k_1} \cdot 100, \tag{9}$$

when it is obvious that the error will be zero if

$$\frac{k_2}{h+k_2} \cdot \frac{c_2}{c_1} = \frac{h}{h+k_1}.$$

Titration by the displacement method, which is based on the reaction between the salt of a weak acid and a strong acid, is usually considered in isolation from the medium in which it is performed. We adopt such an approach, however, only in the case where the solution of the salt is prepared and kept under conditions which exclude CO_2 absorption from the air.

If it is accepted that the solubility of CO_2 in water at room temperature is of the order of $3.8 \cdot 10^{-2}$ mol/liter, then at a concentration of CO_2 in the laboratory air of the order of 0.05 vol.%, it is possible to assume that the equilibrium concentration of CO_2 in any aqueous solution open to the air will be roughly $2 \cdot 10^{-5}$ mol/liter.

Under such conditions a solution of a salt NaA, for which $c_{NaA} = c_{Na^+} = c_{A^-} = c$ represents a complex system described by the equations

$$A^- + H^+ \rightleftarrows HA;$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-;$$

$$H^+ + OH^- \rightleftarrows H_2O.$$

In this system there are 5 unknowns: $[H^+] = x$, $[A^-] = y$, $[HA] = z$, $[HCO_3^-] = u$, $[OH^-] = t$.

Assume that $[H_2CO_3] = a = 2 \cdot 10^{-5}$ mol/liter, $k_{HA} = k$, $k_{H_2CO_3} = k_1 = 3.5 \cdot 10^{-7}$ and $k_{H_2O} = w = 10^{-14}$.

Applying the law of mass action to our three equations, and using the value of the initial concentration of the salt $c_{NaA} = c$, and the principle of the electroneutrality of the solution, we get the following system of equations:

$$xy = kz;$$

$$xu = k_1 a;$$

$$xt = w;$$

$$c = y + z$$

$$c + x = y + u + t.$$

This system reduces to an equation of the third order

$$x^3 + (c + k)x^2 - (ak_1 + w)x - k(ak_1 + w) = 0. \qquad (10)$$

In so far as the hydrogen ion concentration $[H^+]$ in not very dilute aqueous solutions of a salt of a weak acid is very small as compared to the initial concentration of the salt, i.e. $x \ll c$, Equation (10) is transformed into a quadratic

$$(c + k)x^2 - (ak_1 + w)x - k(ak_1 + w) = 0. \qquad (11)$$

With the help of this equation it is possible to calculate the actual pH of a solution of a salt NaA, in equilibrium with air and thence to calculate $[HCO_3^-] = \frac{ak_1}{x}$ and the total concentration of carbonate equal to $\frac{ak_1}{x} + 2 \cdot 10^{-5}$ mol/liter.

Results calculated by this method for 0.1 N solutions of salts of the type NaA of weak acids of different strengths are given in the following table.

TABLE

pH Values and Equilibrium Concentrations of Components in Equilibrium in 0.1 N Solutions of Salts of Weak Acids of the Type NaA, in Contact with Air Containing 0.05 vol.% CO_2

K_{HA}	$[H^+]$	$[A^-]$	$[HA]$	$[HCO_3^-]$	pH, Calculated	
					CO_2 accounted	From hydrolysis of NaA
10^{-5}	$2.6 \cdot 10^{-8}$	$9.97 \cdot 10^{-2}$	$3.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	7.6	9.0
10^{-6}	$8.4 \cdot 10^{-9}$	$9.92 \cdot 10^{-2}$	$8.0 \cdot 10^{-4}$	$8.0 \cdot 10^{-4}$	8.1	9.5
10^{-7}	$2.6 \cdot 10^{-9}$	$9.75 \cdot 10^{-2}$	$2.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	8.6	10.0
10^{-8}	$8.7 \cdot 10^{-10}$	$9.20 \cdot 10^{-2}$	$8.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	9.1	10.5
10^{-9}	$3.0 \cdot 10^{-10}$	$7.70 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$	9.5	11.0
10^{-10}	$1.2 \cdot 10^{-10}$	$4.55 \cdot 10^{-2}$	$5.45 \cdot 10^{-2}$	$5.45 \cdot 10^{-2}$	9.9	11.5

The results given in the table are of importance for the calculation of the amount of carbonates contained in solutions of salts of weak acids both during titration and also for making up buffer solutions.

These results also show that titration by the displacement method is practically always a titration of a complex mixture of two salts NaA and $NaHCO_3$ and acids HA and HCO_3^-. Therefore the theory of titration by the displacement method for one salt is only of significance in special cases.

The titration of a mixture of two salts of weak acids with a solution of strong acid is solved by the same method as that used for investigating the titration of a mixture of two weak acids with an alkali solution. Let $c_{NaA_1} = c_{A_1^-} = c_1$; $c_{NaA_2} = c_{A_2^-} = c_2$; $c_{Na^+} = c_1 + c_2$. At the first stoichiometric point $c_{HA_0} = c_{H^+} = c_{A_0} = c_2$, and at the beginning it can be assumed that $c_{Na^+} = [Na^+] = c_1 + c_2$; $c_{A_1^-} = c_1$; $c_{A_0^-} = [A_0^-] = c_2$ and $c_{HA_2} = c_2$. If the ionic strength of the solution is not taken into account, then it can be assumed that Na^+ and A_0^- ions will not affect the equilibrium. In this case the equilibrium is described by the following equations:

$$HA_2 \rightleftarrows H^+ + A_2^-;$$

$$H^+ + A_1^- \rightleftarrows HA_1;$$

$$H_2O \rightleftarrows H^+ + OH^-$$

and contains 6 unknowns: $[H^+] = x$, $[OH^-] = y$, $[A_1^-] = z$, $[HA_1] = u$, $[A_2^-] = v$, $[HA_2] = t$.

By arranging the system of equations as done previously above and solving it with respect to x, we get an equation of the 4th order.

$$x^4 + (c_1 + k_1 + k_2)x^3 + (c_1k_2 + k_1k_2 - c_2k_2 - w)x^2 - (c_2k_1k_2 + k_1w + k_2w)x - k_1k_2w = 0,$$

which can be used for exact calculation of pH. In determinations of this type c_1 and c_2 should never be less than 0.01 mol/liter. Under these conditions $c_1 \gg x$, k_1, k_2 and our equation can be reduced to the form:

$$x^3 + \frac{k_2(c_1 - c_2) + k_1k_2 - w}{c_1}x^2 - \frac{c_2k_1k_2 + w(k_1 + k_2)}{c_1}x - \frac{k_1k_2w}{c_1} = 0.$$

In these equations the index 1 refers to the stronger acid and the index 2 to the weaker acid. In this case $k_2 < k_1$ and the first stoichiometric point corresponds to the point at which the mixture contains an amount of NaOH equivalent to the initial concentration of the NaA_2.

For the case where c_{HA_0} in the mixture is equal to c, while $c_2 < c < c_1 + c_2$, it is easy to derive the equation:

$$x^4 + (c_1 + c_2 - c + k_1 + k_2)x^3 + [(c_2 - c)k_1 + (c_1 - c)k_2 + k_1k_2 - w]x^2 - (ck_1k_2 + k_1w + k_2w)x - k_1k_2w = 0. \qquad (12)$$

Where $x = [H^+] \ll c_1, c_2, c$, this equation assumes the form:

$$x^3 + \frac{[(c_2 - c)k_1 + (c_1 - c)k_2 + k_1k_2 - w]}{c_1 + c_2 - c + k_1 + k_2}x^2 - \frac{ck_1k_2 + (k_1 + k_2)w}{c_1 + c_2 - c + k_1 + k_2}x - \frac{k_1k_2w}{c_1 + c_2 - c + k_1 + k_2} = 0.$$

The distribution of H^+ ions between the anions A_1^- and A_2^- is solved just as above for the titration of a mixture of two weak acids with alkali. The question of the possible determination of NaA_2 in the presence of NaA_1 is solved by means of the formula:

$$\frac{k_1}{k_2} = \frac{\alpha}{(1-\alpha)^2}\left[\frac{c_1}{c_2} - (1-\alpha)\right],$$

which is derived in the same way as Formula (3) and differs from it only by the ratio $\frac{c_1}{c_2}$.

The solution of the distribution of $z = cv$ mols of acid, added to 1 liter of a mixture containing c_1 mols of NaA_1 and c_2 mols of NaA_2 is achieved by the method given above for the titration of two acids with alkali. From these results it seems that the distribution coefficient

$$\alpha = \frac{hc_2(h + k_1)}{hc_1(h + k_2) + hc_2(h + k_1)}, \qquad (13)$$

but

$$z = cv = \frac{h}{h + k_1} c_1 + \frac{h}{h + k_2} c_2. \qquad (14)$$

The indicator error in this case, as can be seen is equal to

$$\frac{z - c_2}{c_2} \cdot 100 = \left\{\frac{h}{h + k_1} \cdot \frac{c_1}{c_2} - \frac{k_2}{h + k_2}\right\} \cdot 100. \qquad (15)$$

In this case the value of cv is also a linear function of the initial concentrations of the salts c_1 and c_2. Titration to a fixed pH in which cv is taken into account, in this case also ensures the possibility of giving an approximate determination of the composition of a mixture of two salts of weak acids.

SUMMARY

1. General formulas are given for the calculation of the distribution coefficients of alkali between two weak acids or of H^+ ions between the anions of two acids.

2. It has been shown that the amount of strong alkali in the first case and of strong acid in the second case is a linear function of the initial concentrations of the weak acids or their salts.

3. A general method is given for the calculation of equilibrium for a solution of a salt of a weak acid in contact with air containing CO_2. Results are given of such calculations for 0.1 M solutions of salts of weak acids.

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AMPEROMETRIC TITRATION OF NICKEL WITH DIOXIMES

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Organic reagents which enable determinations of individual elements to be made without preliminary separation from other elements present are of great importance in amperometric titration methods. The shape of the titration curve depends on the nature of a given reagent. If the substance to be determined and the reagent give a diffusion current on applying an EMF to both, then the curve obtained will be V-shaped and will enable the equivalence point to be determined with great accuracy. Curves of this type are obtained when dimethylglyoxime, α-benzoinoxime, salicylaldoxime and a number of other reagents are used. In those cases where the reagent does not give a diffusion current on applying an EMF, the titration curves will be of the L form, which is less suitable for the determination of the equivalence point. Up to the present time a considerable amount of work has been done on the application of individual organic reagents in amperometric titration. Zanko [1], Stock [2], Stone and Furman [3] showed the possibility of using oximes for the determination of Mg, Zn, Cu, Al and Cd. The work of I. Kolthof [4] and Mukhina [5] on the use of dimethylglyoxime for the determination of Ni is also known. A number of organic reagents have been suggested for the determination of Cu: α-benzoinoxime (A. Langer [6]), α-nitroso-β-naphthol (I. Kolthof and Langer [7]), salicylaldoxime (A. Neuberger [8]), and quinaldinic acid (Stock [9]).

In the present paper, results are given for the use of dimethylglyoxime and its sodium salt and of the dioxime of cyclohexandioxime. The latter has been shown previously to possess a number of advantages over dimethylglyoxime. The work was carried out by means of a dropping mercury electrode. The concentrations of the Ni and dioxime solutions respectively were determined gravimetrically. $NiSO_4$ was determined by precipitation with dimethylglyoxime and the dioxime by precipitation with Ni salts.

The Use of Dimethylglyoxime and Its Sodium Salt

Determination of Nickel in Solutions of Its Pure Salts. Dimethyl glyoxime as a reagent for Ni was proposed by Chugaev [12], and has been widely used in analytical chemistry, both for the gravimetric and colorimeetric determination of Ni [13]. Some authors use the Na salt of dimethylglyoxime.

An essential condition in performing amperometric titration is the choice of the correct base solution. In this case we considered that the chosen electrolyte could be used for complex formation with Fe and Al. Sodium acetate and tartrate respectively, and sodium and ammonium citrates were considered. The half-wave potential of Ni is −1.1 V. After a number of preliminary experiments, it was established that it is best to titrate Ni in a base solution of 0.1 N Na-acetate for which a clearly defined diffusion wave was obtained. Polarograms obtained for Ni in NH_4-citrate and Na-tartrate did not have a clearly defined form and gave very small wave heights.

Dimethylglyoxime is reduced on the droping mercury electrode as shown by Kolthof [4] and Stromberg [15]. The polarograms were drawn visually and the

EMF checked with a Weston cell; gelatin was used as a maximum suppressor. With a base electrolyte of 0.1 N Na-acetate for a concentration of dimethylglyoxime of 0.002 M, the reduction potential E = −1.13 V and the half-wave potential $E_{1/2}$ = −1.40 V; while for 1 N NH_4OH and 0.1 N NH_4Cl the reduction potential E = = −1.14 V (see Curve 1 in the diagram).

A more clearly defined curve for amperometric titration was obtained when the EMF across the electrolytic cell was increased to a potential greater than the half-wave potential of the element being determined. We used a potential of −1.70 V.

Titrations were invariably carried out in open vessels without removal of oxygen from the solution. The results for titration of pure Ni solutions in a base electrolyte of 0.01 N Na-acetate are given in Table 1.

TABLE 1

Expt. No.	Ni taken in mg	Vol in ml	Ni found in mg	Error in mg
1	0.12	10	0.21	+0.09
2	0.30	10	0.31	+0.01
3	0.60	10	0.63	+0.03
4	1.20	20	1.23	+0.03
5	2.40	20	2.38	−0.02
6	3.60	20	3.57	−0.03

The volume of the titration solution is changed according to the Ni content. In the more dilute solutions the precipitate separates slowly, presumably because of the formation of supersaturated solutions; it is therefore necessary that titrations should be performed with amounts of Ni which are not less than 0.2–0.3 mg in 10 ml.

Determination of Nickel in the Presence of Other Elements. Ni was determined in the presence of Fe, Cr, and Al. It was established that for small amounts of Fe (Ni:Fe = 1:3), titration can be carried out satisfactorily with a base electrolyte of 0.1 N Na-acetate.

With increasing concentration of Fe it becomes necessary to use 2 N Na-acetate, while for even greater amounts of Fe, more than 1:10, it is recommended that the excess Fe should be first removed, preferably in the form of the double salt with NaF [14]. For large concentrations of Fe it is best to take a volume of 40 ml and to increase the concentration of the Na-acetate.

In the titration of mixtures of Ni and Al and of Ni and Cr, exactly the same pattern is observed. For small amounts of Al and Cr the titration is satisfactory when 0.1 N Na-acetate is used as the base electrolyte, but with increasing amounts of Al or Cr to ratios of 1:10 it is recommended that 2 N Na-acetate be used as with Fe.

TABLE 2

Expt. No.	Ni taken in mg	Ni:Fe	Base electrolyte	Vol in ml	Ni found in mg	Error in mg
1	1.20	–	0.1 N sodium acetate	20	1.22	+0.02
2	1.20	1:1	Ditto	20	1.23	+0.03
3	1.20	1:2	"	20	1.22	+0.02
4	1.20	1:3	"	20	1.23	+0.03
5	1.20	1:5	"	20	1.28	+0.08
6	1.20	1:8	2 N sodium acetate	20	1.23	+0.03
7	2.40	1:8	Ditto	40	2.42	+0.02
8	–	1:10	"	40	2.38	−0.02

In the determination of Ni in the presence of considerable amounts of Al and Cr (for ratios of Ni:Cr and Ni:Al = 1:10) equilibrium is only slowly attained after addition of each portion of the reagent.

Titration with a Solution of Sodium-Dimethylglyoxime. The reduction potential of Na-dimethylglyoxime with a base electrolyte of 0.1 N Na-acetate is the same as for dimethylglyoxime itself (see Curve 2 on the diagram). An aqueous solution of Na-dimethylglyoxime was used. A characteristic of this reagent is the rapidity with which Ni can be determined because of the fast rate at which a state of equilibrium is reached during titration.

Titration can be carried out in the presence of Na-acetate and other electrolytes- 0.1 N NaCl and 0.1 N Na_2SO_4. Results are given in Table 3.

TABLE 3

Expt. No.	Ni taken in mg	Base electrolyte	Ni found in mg	Error in mg
1	1.20	0.1 N CH_3CO_2Na	1.21	+0.01
2	2.40	Ditto	2.43	+0.03
3	2.40	0.1 N NaCl	2.41	+0.01
4	2.40	0.1 N Na_2SO_4	2.42	+0.02

On the basis of these results it can be stated that Na-dimethylglyoxime can be substituted for dimethylglyoxime itself.

The Use of Cyclohexanedione-dioxime

Cyclohexanedione-dioxime has been tested as a reagent for Ni both by Peshkova, Gontaeva and Vedernikova [10] and by Johnson and Simmons [11]. Ni-cyclohexanedione-dioxime has a bright red color and is more stable in acid media (pH 3.3) than Ni-dimethylglyoxime. It is also considerably more stable in ammoniacal solutions. These important properties of Ni-cyclohexanedione-dioxime indicate that it will be useful for the determination of Ni in the presence of other metals. A 0.025 M aqueous solution of the reagent was used. It was estimated gravimetrically under conditions established previously.[1)]

The polarograms obtained with this reagent in a base electrolyte of 0.1 N Na-acetate show that its reduction potential E = −1.14 V and its half wave potential $E_{1/2}$ = −1.40 V, as for dimethylglyoxime (see curve 3 in the diagram). From experiments on the determination of Ni with cyclohexanedione-dioxime in solutions of pure Ni salts in the presence of different electrolytes, it was shown that a solution of Na-acetate or of the sulfate of an alkali metal in the presence of ammonia could be used as base electrolytes. From Table 4 it can be seen that the determination of Ni with this reagent can be carried out with an ammoniacal complex, which distinguishes it from dimethylglyoxime.

Titration of Nickel in the Presence of Zinc. The possibility of determining Ni with cyclohexanedione-dioxime in ammoniacal solution is of particular interest for the use of this reagent in the titration of Ni in the presence of Zn, since the

1) The reagent was made in Prof. A. P. Terentev's laboratory (Moscow State University) by A. I. Guseva by a method developed at the Institute for Chemical Reagents).

TABLE 4

Expt. No.	Ni taken in mg	Base Electrolyte	Vol., in ml	Ni found in mg	Error in mg
1	0.77	0.1N CH_3CO_2Na	10	0.77	0
2	1.55	Ditto	20	1.55	0
3	1.55	0.1N K_2SO_4 + 1 ml 10% NH_4OH	20	1.55	0
4	1.55	0.1N K_2SO_4 + 5 ml 10% NH_4OH	20	1.58	+0.03

latter combines to form an ammoniacal complex and does not interfere with the determination of Ni.

Under these conditions a clearly defined curve is obtained which gives reproducible equivalence points.

The results in Table 5 show that an excess of 1 ml NH_3 is sufficient. 0.1 N Na-acetate was used as the base electrolyte.

TABLE 5

Amount of Ni 1.55 mg, vol. 20 ml, NH_4OH 10%

Expt. No.	Ni:Zn	Base Electrolyte	Ni found in mg	Error in mg
1	-	0.1N CH_3CO_2Na	1.55	0
2	1:5	0.1N CH_3CO_2Na + 1 ml NH_4OH	1.50	−0.05
3	1:5	0.1N CH_3CO_2Na + 5 ml NH_4OH	1.57	+0.02
4	1:7	Ditto	1.53	−0.02
5	1:10	"	1.55	0.00
6	1:15	"	1.63	+0.08
7	1:15	0.1N CH_3CO_2Na + 7 ml NH_4OH	1.55	0.00
8	1:20	0.1N CH_3CO_2Na + 10 ml NH_4OH	1.57	+0.02
9	1:50	0.1N CH_3CO_2Na + 12 ml NH_4OH	1.54	−0.01

Titration of Nickel with Cyclohexanedione-Dioxime in the Presence of Aluminum and Iron. After a number of preliminary experiments it was established that in the presence of Al, Ni can be titrated with sufficient accuracy if Na-tartrate with added ammonia was used as the base electrolyte. Under these conditions Al and Ni are in the form of complex compounds.

In contrast to titration of Ni with dimethylglyoxime with Na-tartrate with added ammonia as base electrolytes, titration with cyclohexanedione-dioxime proceeds without any complications because the precipitate separates rapidly.

The obvious reason is the smaller solubility of Ni-cyclohexanedione-dioxime as compared with Ni-dimethylglyoxime.

Satisfactory results were obtained for ratios of Ni:Al from 1:1 to 1:70.

Favorable results for the determination of Ni in the presence of Fe were obtained with either Na-acetate or Na-citrate as base electrolytes, ammonia being added in both cases. Results are given in Table 7.

Complete satisfactory results were obtained for ratios of Ni:Fe of 1:60; results in Table 7 show that, at ratios of Ni:Fe = 1:20 and over that, Fe probably

TABLE 6

Amount of Ni 1.55 mg, vol. 20 ml, base electrolyte in all the experiments 4 ml saturated sodium acetate $Na_2C_4H_4O_6$ + 4 ml of 10% NH_4OH

Expt. No.	Ni:Al	Ni found in mg	Error in mg
1	1:12	1.53	−0.02
2	1:20	1.55	0.00
3	1:30	1.53	−0.02
4	1:50	1.54	−0.01
5	1:70	1.58	+0.03

forms a stable complex compound with Na-citrate. All these results show that cyclohexanedione-dioxime has definite advantages over dimethylglyoxime, in that it gives a compound with Ni which is characterized by a greater stability in ammoniacal media, which enables Ni to be determined in the presence of large amounts of Fe and Al, and enables Ni to be determined in the presence of Zn as well.

Use of α-Furildioxime

α-Furildioxime was investigated by V. M. Peshkova for use in the gravimetric and colorimetric determination of Ni. In the present work a 0.012 M alcoholic solution of this reagent was used. α-Furildioxime gives a reddish-terracotta colored precipitate with Ni. The reduction potential of the reagent in a base electrolyte of 0.1 N Na-acetate was found to be E = −1.14 V and its half wave potential $E_{1/2}$ = −1.40 V.

This reagent is not suitable for the amperometric titration of Ni since the precipitate does not form readily and only slowly coagulates at room temperature.

TABLE 7

Amount of Ni 1.05 mg, vol. 20 ml, NH_4OH 10%

Expt. No.	Ni:Fe	Base Electrolyte	Ni found in mg	Error in mg
1	1:4	0.1N CH_3CO_2Na + 1 ml NH_4OH	1.55	0.00
2	1:10	1N CH_3CO_2Na + 1 ml NH_4OH	1.56	+0.01
3	1:20	2N CH_3CO_2Na + 1 ml NH_4OH	1.51	−0.04
4	1:20	4 ml saturated sodium citrate + 1 ml NH_4OH	1.55	0.00
5	1:40	Ditto	1.56	+0.01
6	1:60	"	1.60	+0.05

TABLE 8

Alloy used	Elemental composition, %					Ni determined amperometrically
	Ni	Fe	Cr	Al	Mn	
Chromenickel steel	8.33	73.70	18.00	–	–	8.30 8.24
Manganesenickel alloy	76.50	–	–	2.00	23.50	76.20
Nickelaluminum alloy	98.00	–	–	–	–	98.70
Nichrome	60.00	20.0	20.0	–	–	60.08 60.02
Electroresistance steel	10.00	77.0	13.0	–	–	9.93 10.02

The results obtained by the methods described above were checked by analyses of several samples of Ni alloys of known composition.

Results given in Table 8 show that Ni can be determined by amperometric titration fairly accurately in alloys containing up to 60% Ni.

SUMMARY

1. Dimethylglyoxime, Na-dimethylglyoxime and cyclohexanedione-dioxime can be used for the amperometric titration of Ni in pure Ni salts and in the presence of Fe^{3+}, Al^{3+}, Cr^{3+} and Zn^{2+}.

2. For titration with dimethylglyoxime, Na-acetate is recommended as the base electrolyte.

3. Titration can be carried out at room temperature without the necessity of excludion of oxygen from the solution.

4. Cyclohexanedione-dioxime is preferred to dimethylglyoxime and Na-dimethylglyoxime because it can be used for the determination of Ni in the presence of large amounts of Al, Fe, Cr and Zn^{2+}.

5. It has been confirmed by amperometric titration that Ni-cyclohexanedione-dioxime is more stable than Ni-dimethylglyoxime.

6. It has been established that the dioximes tested are reduced at the same potential; the half wave potential $E_{1/2} = -1.40$ V.

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THE CONDUCTOMETRIC TITRATION OF ZINC WITH BARIUM HYDROXIDE

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The conductometric titration of Zn with $Ba(OH)_2$ has been described by Kolthof [1]. Kolthof showed that as the result of the formation of basic salts the electroconductivity changes with time and the method does not seem to be sufficiently accurate. With time the electroconductivity can often change continuously as a result of the adsorption of ions on the precipitate which separates out. In order to elucidate the reasons for the change of electroconductivity with time during the titration of Zn ions with $Ba(OH)_2$ it is necessary therefore to exclude the effect of adsorption by precipitate ions. To do this, the titration of Zn should be carried out in the presence of some material which will be preferentially adsorbed on the precipitate which separates out before the Zn ions and the ions of the reagent added. $KMnO_4$ can be used for this purpose, since in its presence, as shown by preliminary experiments, a colored precipitate of zinc hydroxide and $BaSO_4$ can be obtained [2]. Consequently, during the conductometric titration of $ZnSO_4$ with $Ba(OH)_2$ in the presence of $KMnO_4$ it is to be expected that permanganate ions will be preferentially adsorbed on the precipitates of zinc hydroxide and $BaSO_4$ formed.

It was shown experimentally that on titrating solutions of $ZnSO_4$, addition of each portion of excess reagent leads to a continuous change in the electroconductivity after the equivalence point has been reached. This hampers the titration, and in the case of very weak solutions, makes titration impossible. If the $ZnSO_4$ is titrated in the presence of $KMnO_4$ the electroconductivity does not change with time. This fact is the basis of the method for the determination of Zn ions with $Ba(OH)_2$ described below.

30 ml of aqueous $ZnSO_4$ was placed in the vessel for conductometric titration, and a small amount of well washed, dry (old) $BaSO_4$ and 1-2 ml of a saturated $KMnO_4$ solution added. The solution was carefully stirred and conductometrically titrated with $Ba(OH)_2$. The $Ba(OH)_2$ was titrated against a solution of $ZnSO_4$ of known concentration (Table 1).

Aqueous solutions of $ZnSO_4$ can be titrated at concentrations of 0.01 N. At lower concentrations the experimental error increases considerably. It should be noted that when $ZnSO_4$ is titrated by the method described a change of the electroconductivity with time is still observed. This occurs when a lot of precipitate settles out and the amount of $KMnO_4$ is insufficient; in such a case the amount of $KMnO_4$ should be increased until it is considerably greater than the amount adsorbed on the precipitate which settles out. Only in such a case where adsorption of permanganate ions occurs will the change in concentration of these ions in the solution be small and not affect the magnitude of the electroconductivity.

When very dilute solutions of $ZnSO_4$ are titrated the electroconductivity can change with time as a result of the slow crystallization of the $BaSO_4$ precipitated. Results of titrations can be improved by the addition of dry $BaSO_4$, which will hinder the formation of super-saturated solutions.

The same method can be used for the titration of Zn-chloride, nitrate and acetate respectively, but the shape of the curves obtained will differ from that

obtained with $ZnSO_4$. When $ZnSO_4$ is titrated with $Ba(OH)_2$ the Zn ions separate from solution by forming a hydrated zinc oxide, while the SO_4 ions are removed as $BaSO_4$. As a result, up to the equivalence point the electroconductivity will drop rapidly. After the equivalence point, the Ba and OH ions appear and considerably increase the electroconductivity. The conductometric curve for $ZnSO_4$ will therefore have an acute angle. When Zn-chloride, nitrate or acetate are titrated with $Ba(OH)_2$, only the Zn ions are precipitated from solution, while instead of these the less mobile Ba ions are formed. In these cases, therefore, the electro conductivity will not drop so rapidly and the angle between the two branches of the curve will be obtuse, so that determination of the equivalence point by means of such a curve will be subject to rather large errors.

Titration of dilute solutions of Zn-chloride, nitrate or acetate is accompanied by a change in the electroconductivity with time, which hampers the determination of the equivalence point. Nevertheless, in the presence of $KMnO_4$, the equivalence point can still be found with a fair degree of accuracy as the results in Tables 2,3 and 4 show. Solutions of Zn-chloride, nitrate and acetate with concentrations less than 0.002 N can be titrated with an error of ca.1%. Cd and Cu interfere with the determination of Zn.

By this method solutions of $ZnSO_4$ containing small amounts of $CuSO_4$ can be titrated. In order to do this it is necessary to remove the Cu ions in the form of some insoluble compound, e.g. the iodide.

TABLE 1

$ZnSO_4$

Taken in mg	Found in mg	Error in %
20.94	20.91	0.2
15.70	15.67	0.2
10.47	10.80	3.1

TABLE 2

$Zn(CH_3COO)_2$

Taken in mg	Found in mg	Error in %
16.63	16.63	0.0
11.09	11.12	0.3
5.54	5.58	0.7
1.85	1.95	5.7

TABLE 3

$Zn(NO_3)_2$

Taken in mg	Found in mg	Error in %
11.97	11.97	0.0
7.18	7.19	0.2
1.19	1.21	1.7

TABLE 4

$ZnCl_2$

Taken in mg	Found in mg	Error in %
11.07	11.10	0.3
6.92	6.93	0.2
2.77	2.79	0.8

Before titrating solutions of $ZnSO_4$ containing $CuSO_4$, it is necessary to add another adsorbent instead of $KMnO_4$, viz.a saturated solution of methylene violet. A dry precipitate of $BaSO_4$ is also added. In order to avoid separation of free iodine, a few drops of Na-thiosulfate is added to the solution followed by a few drops of KI. The solution is subsequently stirred thoroughly and conductometrically titrated with $Ba(OH)_2$. Results are given in Table 5.

It has been previously observed that on titration of Zn-chloride, nitrate, or acetate with $Ba(OH)_2$, the respective Ba salt is formed. Being good electrolytes they considerably increase the electroconductivity of the solution at the equivalence point, so that the angle between the two branches of the conductometric curve becomes considerably greater than that of the conductometric curve for $ZnSO_4$. From this it follows that the angle between the two branches of the curve will be greater the higher the conductivity of the solution at the equivalence point. Therefore, in the titration of $ZnSO_4$ with $Ba(OH)_2$ in the presence of Cu ions, the angle between

the branches of the curve will increase since electrolytes (KI and $Na_2S_2O_3$) are added before titration which increase the electroconductivity at the equivalence point considerably. This in turn leads to a greater experimental error.

In cases where the $ZnSO_4$ solution contains large amounts of Cu it is necessary to increase the amount of thiosulfate and KI; this leads to an increase in the angle between the two branches of the conductometric curve and consequently to a greater experimental error. In order that the increase in experimental error be as small as possible, it is recommended that use of excess KI and $Na_2S_2O_3$ be avoided. The necessary amount can be determined by preliminary experiments. If titrations are made in the absence of methylene violet, low results are obtained.

Special attention should be given to the cleanliness of the titration vessel; care should be taken to remove precipitated Zn hydroxide and $BaSO_4$, which separates out on the walls and on the electrodes.

TABLE 5

Determination of Ni in Mixtures of Zinc and Copper Sulfates

Taken, in mg		Found Zn, in mg	Error, in %
Zn	Cu		
76.8	4.1	76.6	0.3
76.8	20.7	76.4	0.5
76.8	41.3	76.1	0.9
76.8	82.6	75.7	1.4

SUMMARY

A method for the titration of Zn salts with $Ba(OH)_2$ has been proposed. It has been established that in the titration of aqueous solutions of $ZnSO_4$ down to concentrations of 0.01 N, the electroconductivity changes with time after addition of the reagent, mainly because of the adsorption of ions of the added reagent and the precipitate formed. It has been shown that Zn can be titrated in the presence of small amounts of Cu.

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CONDUCTOMETRIC DETERMINATION OF POTASSIUM BY MEANS OF SODIUM PICRATE

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Potassium is usually determined by means of the chloroplatinate, perchlorate, and cobaltonitrite methods. Among other methods, the polarographic, colorimetric, and refractometric methods may be mentioned. The conductometric method is rarely used because the precipitate crystals form slowly, so that the electroconductivity of the solution changes with time over a prolonged period.

Of the conductometric methods for the determination of potassium known to us the following may be mentioned. Jander and Pfundt [1] recommend titration of potassium conductometrically with sodium perchlorate at 0°. The authors note that the electroconductivity of the solution does not stabilize immediately after addition of the reagent, because of the slow crystallization of the precipitate.

Winkel and Maas [2] titrated potassium salts conductometrically with dipicrylamine. This was effected by precipitating the potassium by addition of a soluble picrylamine salt, dissolving the filtered precipitate in acetone, diluting with water to a final acetone concentration of 20-30% and titrating with 0.1 N HCl or 0.01 N naphthalene-α-sulfonic acid. The accuracy of their method was ±0.5%. It was noted that after addition of the first portion of acid the electroconductivity changed slowly with time because of the slow crystallization of the dipicrylamine which separated out. This change in the electroconductivity persisted until a sufficient number of crystals had formed, after which addition of reagent did not lead to a change of electroconductivity with time. It is possible to precipitate potassium by titrating it against a known amount of an aqueous solution of soluble salt of dipicrylamine, such as the magnesium salt. The filtrate containing excess of the soluble salt of dipicrylamine is then titrated with acid, when the dipicrylamine formed separates out as a precipitate.

Portnov and Afanasev [3] titrated potassium in an aqueous-alcoholic medium with a solution of fluosilicic acid conductometrically. The electroconductivity changes with time as a result of the slow formation of precipitate. The accuracy of this method was 2-2.5%. These authors changed the indirect method of Winkel and Maas for the determination of potassium. The accuracy varied from 0.6 to 1.5% according to the amount of potassium.

We propose that sodium picrate be used for the determination of potassium. Titration is carried out in aqueous solution, since preliminary experiments showed that titration in alcoholic solution did not improve the results.

The experimental method is briefly as follows. A known volume of the standard sodium picrate solution is placed in the vessel for titration, and a small amount of dry potassium picrate added. The test solution containing potassium chloride and sodium chloride is then added. The solution is carefully mixed and the excess sodium picrate backtitrated with potassium chloride of known strength. When this method is used the electroconductivity reaches its equilibrium value immediately after addition of the reagent.

The sodium picrate solution used as reagent was prepared by diluting a saturated solution of it to twice its volume with distilled water. The strength

of this solution was established by conductometric titration of a known volume of the sodium picrate solution with a solution of standard potassium chloride in the presence of a small amount of dry potassium picrate which is added to the solution.

Results obtained for the determination of potassium by the method described above (Table 1) show that the experimental error is approximately 2%. According to Table 2 any sodium chloride present does not interfere with the determination.

TABLE 1

Determination of potassium with sodium picrate

KCl		Error
Taken in mg	Found in mg	in %
56.20	56.00	0.4
80.30	79.30	1.2
105.50	105.59	0.08
120.58	122.23	1.3
150.72	152.53	1.2

TABLE 2

Determination of potassium in the presence of sodium

Taken in mg		mg KCl	Error
KCl	NaCl	found	in %
84.3	11.5	84.2	0.2
81.1	23.0	81.0	0.2
105.5	11.2	107.3	1.7
105.5	22.4	105.6	0.1
105.5	33.6	107.4	1.7
105.5	44.8	106.4	0.8
105.5	67.2	105.3	0.2

The method described can be used for mass determinations of potassium in different samples. A known weight of test sample is dissolved and, after separation of the accompanying cations, the alkali metals remaining are converted into the chlorides. The latter are dissolved in a small amount of distilled water and added to the sodium picrate solution. The excess sodium picrate is then determined as described above. The error of the method suggested for determination of potassium is of the same order as the fluosilicic and dipicrylamine methods. The advantages of this method are: a low temperature thermostat as used in the perchlorate method is unnecessary; no alcohol is required as in the fluosilicic method; no filtration is necessary as in the dipicrylamine method.

SUMMARY

A method is proposed for the determination of potassium by means of sodium picrate. The method consists in adding a known amount of test solution to a known amount of the reagent solution – sodium picrate – excess of which is back-titrated with potassium chloride. It has been shown that sodium ions present in the test solution do not interfere with the potassium determination.

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THE CHRONOMETRIC DETERMINATION OF ELECTROLYTE CONCENTRATIONS

1. DETERMINATION OF THE CONCENTRATIONS OF THIOSULFATE AND ACID IN THEIR REACTION MIXTURE

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Many reactions in which organic materials participate proceed fairly slowly. In such cases it is expedient to carry out determinations on the concentration of reactants at definite time intervals from the amounts of reaction products formed. When a precipitate is formed it is very convenient to use a chronometric method for the determination of the concentrations of the organic reagents [1].

This method is also applicable for reactions between organic and inorganic compounds. Thus the reactions between aldehydes and ammonia [2] or methyl ketones with iodine [3,4] are used for this purpose. In such cases the quantitative determination of both the organic and mineral compounds is possible.

Nevertheless, the application of this rapid method for the determination of the concentration of only the mineral components during their mutual interaction has not yet been realized. The present communication is devoted to a number of investigations along these lines.

In order to develop our method of investigation we decided to concentrate on the reaction between thiosulfate and acid as being the most suitable for the purpose in view. When thiosulfate reacts with acid there is an induction period, as a consequence of which the turbidity which develops because of the formation of sulfur does not occur immediately. This time can be measured by a stop watch and consequently the chronometric principle can be used for the determination of the concentration of one of these reactants.

EXPERIMENTAL

Determination of the Concentration of Thiosulfate Solutions. Normal solutions of HCl and $Na_2S_2O_3$ were used as the base solutions. The other solutions used were prepared from these by dilution to the requisite concentrations.

The method used was as follows: 1 ml of the thiosulfate solution was mixed with 1 ml of acid and the time from the initiation of the reaction to the moment when turbidity appears was measured with a stop watch.

For increasing the accuracy of the results we used standard turbidities prepared as described by Nikitin and Vershinsky [5].

The results of the concentration of thiosulfate solutions as determined by reaction with hydrochloric acid are given in Table 1.

If the results given in Table 1 for the velocity with which the given mixtures become turbid are represented graphically, with the thiosulfate concentration along the X-axis (in g-equiv./liter) and the time from the beginning of the reaction to the onset of turbidity along the Y-axis, then turbidity isotherms are obtained as shown in Fig. 1.

However, if the inverse value of the thiosulfate concentration is used as in Nikitin's method [1], i.e. the degree of dilution, the turbidity isotherms of Fig. 1 assume a totally different form (Fig. 2).

TABLE 1

Rate with which Mixtures of Thiosulfate and Hydrochloric Acid become Turbid in Relation to Thiosulfate Concentration; t° = 14.5°

Expt. No.	Conc. of thiosulfate in g-equiv./liter	Turbidity velocity, in seconds					
		I	II	III	IV	V	Mean
1	1.000	9.6	9.2	9.0	9.4	9.2	9.30
2	0.833	10.8	10.8	10.6	10.6	10.6	10.70
3	0.750	12.8	12.2	12.0	11.8	12.2	12.10
4	0.666	13.3	13.3	12.2	13.0	13.0	13.14
5	0.500	17.3	17.5	17.0	17.0	17.2	17.20
6	0.417	20.7	20.3	20.8	20.4	20.4	20.50
7	0.375	22.8	22.8	22.4	22.2	22.3	22.50
8	0.333	25.3	25.6	25.0	25.4	25.2	25.30
9	0.250	34.0	33.4	32.3	34.0	32.9	33.50

Here (Fig.2) the value of z, which expresses the supplementary volume of solvent necessary to dilute the control (base solution), to a definite concentration is plotted horizontally.

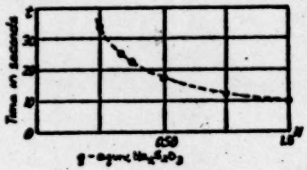

Fig.1. Turbidity isotherm for mixtures of HCl + $Na_2S_2O_3$.

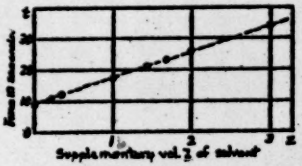

Fig.2. Turbidity isotherm for mixtures of HCl + $Na_2S_2O_3$ when degree of dilution is plotted along the composition axis.

If one volume of control solution is diluted n times, then the ratio of the concentration of this solution to the initial concentration is expressed by the relation:

$$\frac{c}{x} = n. \qquad (1)$$

This signifies that the volume z of the added solvent to give a definite dilution can easily be calculated from the relation

$$n = 1 + z. \qquad (2)$$

Results are given for the calculation of z for the solutions of Table 1, in Table 2.

These values of z are also plotted along the "composition" axis in Fig.2.

The linear form of the turbidity isotherm simplifies the method of determining the concentration of thiosulfate solutions [1]. We prepared a control (base)

solution of thiosulfate for which the velocity of development of turbidity t_1 was determined on interaction with acid. After dilution to twice its volume with water, the new velocity t_2 was determined. The velocity was then determined for a test solution in exactly the same way, t_x. From an equation for the straight line with two known points:

$$\frac{z - z_1}{z_2 - z_1} = \frac{v_x - v_1}{v_2 - v_1}, \qquad (3)$$

for $z_1 = 0$ and $z_2 = 1$, we get:

$$z = \frac{v_x - v_1}{v_2 - v_1}. \qquad (4)$$

TABLE 2

Calculated Values of z for Thiosulfate Solutions

Conc. of thiosulfate in g-equiv./liter	1.000	0.888	0.750	0.666	0.500	0.417	0.375	0.333	0.250
z = n - 1	0	0.20	0.33	0.50	1.00	1.42	1.67	2.00	3.00

Consequently, the value of z was determined from experimental results. By substitution in Equation (1) of the value of n from Equation (2), we get

$$\frac{c}{x} = 1 + z. \qquad (5)$$

The value of z from Equation (4) is substituted in Equation (5):

$$\frac{c}{x} = 1 + \frac{v_x - v_1}{v_2 - v_1}. \qquad (6)$$

From this we obtain the final equation for calculation of the concentrations:

$$x = \frac{c}{1 - \frac{v_x - v_1}{v_2 - v_1}}. \qquad (6a)$$

Results for determinations of the concentration of sodium thiosulfate solutions in reaction mixtures with hydrochloric acid are given in Table 3.

From this table it is clear that this rapid method which we have described for determining the concentration of sodium thiosulfate solutions gives completely satisfactory results. When other acids are used for this reaction, similar results were obtained.

Determination of Acid Concentration. In order to determine the order of the chemical reaction considered with respect to acid we carried out a number of experiments in which the acid concentration was varied. The results for the determination of the velocity of development of turbidity of the reacting mixtures are given in Table 4.

The results given in Table 4 are represented graphically in Fig. 3.

Fig. 3 was drawn in the same way as Fig.2, i.e. the degree of dilution by addition of z volumes of solvent was plotted along the composition axis. The isotherm obtained (Fig.3) shows that the change in concentration of acid from 4.0-0.0312 N has practically no effect on the reaction velocity (velocity of development of turbidity); the isotherm is parallel to the abscissa for the concentrations indicated. It is only below concentrations of 0.0312 N that the

straight line isotherm starts to curve upwards steeply.

This break in the curve occurs at ratios of acid to thiosulfate not greater than 0.03 equiv. to 1 equiv thiosulfate.

Thus, determination of acid by this method (i.e. by reaction with thiosulfate) is possible only in those cases where the concentration of thiosulfate will be several times greater than that of the acid.

If a solution 0.0312 N with respect to acid is used as the base sol for lower concentrations, it is easy to determine the concentration of the acid by the velocity of turbidity development by reacting the solution with thiosulfate. Results for the determination of hydrochloric acid concentration by reacting solutions with thiosulfate are given in Table 5.

TABLE 3

Relative Errors in the Determination of the Concentration of Thiosulfate Solutions

Expt. No.	Concentration of thiosulfate taken in g-equiv/liter	Concentration of thiosulfate found in g-equiv/liter	Relative error
1	1.000	Blank 1	
2	0.832	0.850	+2.04
3	0.750	0.728	-1.60
4	0.666	0.673	+1.05
5	0.500	Blank 2	
6	0.418	0.414	+0.24
7	0.375	0.374	-0.27
8	0.338	0.330	-0.9
9	0.250	0.246	-1.6

TABLE 4

Rate with which Mixtures of Thiosulfate and Hydrochloric Acid become Turbid in Relation to Acid Concentration. t = 19°

Expt. No.	Concentration of acid in g-equiv./liter	Turbidity velocity in seconds			
		I	II	III	Mean
1	4.00000	6.0	6.2	6.0	6.0
2	2.00000	6.0	5.9	6.0	6.0
3	1.00000	6.3	6.1	6.0	6.1
4	0.50000	7.0	6.4	6.6	6.7
5	0.25000	7.0	7.0	6.0	6.3
6	0.12500	6.5	6.9	6.8	6.7
7	0.06250	7.2	7.4	6.9	7.2
8	0.03120	7.2	7.2	6.6	7.0
9	0.01560	8.8	8.9	9.0	8.8
10	0.00780	12.2	11.8	12.4	12.2
11	0.00390	20.0	20.3	18.7	19.9
12	0.00195	34.0	33.2	32.8	33.3

SUMMARY

1. The reaction velocity between thiosulfate and acid in relation to the concentrations of the components was studied by a chronometric method.

TABLE 5

Results of the Chronometric Determination of Concentrations of Acid by Reaction with Thiosulfate

Expt. No.	Concentration taken in g-equiv/liter	Concentration found in g-equiv/liter	Relative error in %
1	0.03120	Blank 1	
2	0.01560	Blank 2	
3	0.00780	0.00800	+2.5
4	0.00390	0.00382	-2.0
5	0.00195	0.00200	+3.0

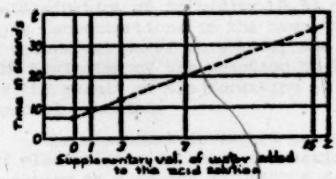

Fig. 3. Turbidity isotherm for HCl + $Na_2S_2O_3$ mixtures when dilutions of the acid solution are plotted on the composition axis.

2. The turbidity isotherms obtained have been investigated and their analytical applications indicated.

3. A characteristic of the reaction was discovered, viz. that up to a certain concentration limit the reaction is of zero order with respect to acid.

4. The method described for the determination of electrolyte concentration can be used for all reactions for which an induction period can be observed. i.e. the time from the beginning of the reaction to the development of turbidity, or color, etc.

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CHRONOMETRIC DETERMINATION OF ELECTROLYTE CONCENTRATIONS

2. DETERMINATION OF SULFITE AND IODATE CONCENTRATIONS IN THEIR ACIDIFIED REACTION MIXTURES

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In our first paper [1] we showed how a rapid chronometric method for the determination of turbidity [2,3] could be applied to the determination of electrolyte concentrations in the case of sodium thiosulfate and hydrochloric acid. In a determination of this kind, the time is measured (by means of a stop watch) from the beginning of the reaction to the moment at which turbidity is first manifested as the result of the formation of sulfur and the concentrations calculated from a special equation.

The chronometric method can also be used for the quantitative determination of electrolytes in colored reactions, where the time from the beginning of the reaction to a moment at which a definite color starts to develop can be measured with a stop watch. One of the reactions of this type which is of particular importance is that between HIO_3 and H_2SO_3. This reaction has been studied from the point of view of its mechanism and its external effects by Landolt [4]. This valuable reaction has a considerable induction period (the length of time from the beginning of the reaction to the appearance of free iodine); the iodine slowly turns starch blue.

The final result of a number of reactions is

$$5H_2SO_3 + 2HIO_3 = 5H_2SO_4 + H_2O + I_2.$$

The separate stages of which are as follows:

1) $3H_2SO_3 + HIO_3 = 3H_2SO_4 + HI$;

2) $5HI + HIO_3 = 3H_2O + 3I_2$;

3) $H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$.

This implies that iodine can only be liberated in significant amounts when the H_2SO_3 has already been used up. Thus iodine is evolved (colors the starch) only when there is a sufficient excess of HIO_3 as an oxidizing agent. The time from the beginning of the reaction to the moment when the mixture becomes colored (the mixture becomes colored throughout its volume simultaneously) can be very accurately measured with a stop watch; the induction period depends both on the concentration of HIO_3 and H_2SO_3 and on other factors.

As far as we know no investigator has used this reaction for analytical purposes. In our opinion, nevertheless, it can be used for the quantitative determination of the original reactants themselves and of other compounds.

What it amounts to is that any substance which can participate in the oxidation-reduction process can affect the induction period of the reaction. The induction period will vary according to the amount of the compounds added. The study of the effect of the concentration of these added compounds is the chief purpose of this investigation.

On practical grounds we thought it more expedient to use KIO_3 and Na_2SO_3 in preference to the free acids (HIO_3 and H_2SO_3).

Since the reaction between the anions IO_3^- and SO_3^{2-} is only possible in acid media, we first studied the effect of different concentrations of H_2SO_4 on the reaction velocity. In addition it was necessary to determine the effect of the concentrations of the reactants themselves.

The present paper is devoted to a description of the effect of H_2SO_4, KIO_3 and Na_2SO_3 on the induction period. A chronometric method for the determination of KIO_3 and Na_2SO_3 in solution is suggested.

EXPERIMENTAL

Effect of Acid Concentration on the Reaction Velocity. The part played by acid in this reaction is not restricted to the process of liberating H_2SO_3 and HIO_3, since the hydrogen ion concentration should also be of considerable importance in exerting a catalytic effect on the reaction. Thus, in the determination of Cl^-, together with Br^- and I^- with $NaBrO_3$ in the presence of H_2SO_4 by Berg's method [5], when 1.5 N H_2SO_4 is used only the Br^- and I^- ions are oxidized, while only a small proportion of the Cl ions are oxidized. It should be noted that at this high concentration of H_2SO_4, the optimum concentrations of the halides themselves in this determination lie within the limit 0.01-0.1 N [5].

We prepared 0.002 M aqueous solutions of KIO_3 and 0.005 M aqueous solutions of Na_2SO_3. The H_2SO_4 solutions vary from 0.5-0.3125 M. All solutions were prepared with doubly distilled water. The reaction was carried out as follows: 1 ml of KIO_3 solution was mixed in a test tube with 1 ml of Na_2SO_3 solution and 2 drops of starch solution; to this mixture was added 1 ml of the H_2SO_4 solution. After shaking the mixture for some time a blue color suddenly appears throughout the volume of the liquid. The time from the beginning of the reaction, i.e. from the moment when acid is added, to the time when color first appears was measured with a stop watch. Since the time taken to add the acid from pipette to test tube has a considerable effect on the accuracy of the measurements, we used a special pipette for introducing the acid whereby the acid was always blown into the reaction mixture with the same velocity.

TABLE 1

The Effect of Sulfuric Acid Concentration on the Reaction Velocity between Potassium Iodate and Sodium Sulfite

Expt. No.	Conc. of H_2SO_4 in mole/liter	Induction period in seconds			
		1	2	3	Mean
1	0.50000	6.8	6.8	6.7	6.76
2	0.25000	11.8	11.7	11.8	11.76
3	0.12500	20.6	20.2	20.5	20.43
4	0.06250	36.8	36.8	37.0	36.87
5	0.03125	68.8	69.0	68.8	68.87

Results for the measurement of the induction period for different acid concentrations are given in Table 1.

By a comparison of the induction periods for this reaction at different concentrations of H_2SO_4, it can be concluded that the reaction velocity is linearly related to the acid concentration.

Effect of the Iodate Concentration. Since the reaction between H_2SO_3 and H_2SO_3 proceeds according to the equation

$$5H_2SO_3 + 2HIO_3 = 5H_2SO_4 + I_2 + H_2O,$$

it follows that the molar ratio of sulfite to iodate is of decisive importance in this case. On increasing this ratio no iodine at all is evolved. The reaction will proceed only for such changes in the concentration of reactants for which the molar ratio of sulfite to iodate will decrease. This means that there are only two possibilities: to decrease the concentration of sulfite for a constant iodate concentration; or to increase the iodate concentration from the critical molar ratio for a constant sulfite ratio.

In Landolt's work on the study of the velocity of this particular reaction some experimental data is given on this question which is of interest to us. This author in his study of the law of mass action for this reaction, changed the concentration of HIO_3, while leaving the H_2SO_4 concentration constant throughout.

For our analytical purposes we examined the relations between the values of the HIO_3 concentrations in Landolt's experiments and the induction periods which he observed for the respective solutions. Since the induction period in a given case is not related by a simple expression to the concentration of the HIO_3, in our calculations we used a method proposed previously by Nikitin in his colorimetric investigation of the reaction velocity of the condensation of carbonyl compounds [6]. He used the equation:

$$\frac{x}{c} = \left(\frac{h_c}{h_x}\right)^n, \qquad (1)$$

where h is the height on the colorimeter scale, i.e., the reciprocal of the intensity. Having established the value of the index n for the reaction he studied, Nikitin derived the corresponding equations for calculating the requisite concentrations.

The molar concentrations of HIO_3 (for constant concentration of H_2SO_4) and the values of the respective induction periods from Landolt's paper are reproduced in Table 2. In addition the values of n which were calculated from the equation below are given:

$$\frac{c_1}{c_2} = \left(\frac{t_2}{t_1}\right)^n, \qquad (2)$$

from which

$$n = \frac{\log c_1 - \log c_2}{\log t_2 - \log t_1}. \qquad (3)$$

TABLE 2

Comparison of the Induction Periods of Solutions with Different Concentrations of HIO_3

Expt. No.	Concentration in mole /liter·10^3		Induction period for comparable solutions		$n = \frac{\log c_1 - \log c_2}{\log t_2 - \log t_1}$	Average value of n
	c_1	c_2	t_1	t_2		
1	2.226	3.338	55.98	28.36	0.595	0.60
2	2.226	4.450	55.98	17.80	0.604	
3	2.226	5.562	55.98	12.24	0.602	
4	2.226	6.673	55.98	9.08	0.603	
5	2.226	7.783	55.98	7.07	0.609	
6	2.226	8.893	55.98	5.55	0.599	

Consequently the value of n necessary for calculating the concentration of HIO_3 has a mean of ca.0.6 and the equations for calculating the concentration will therefore be of the form

$$x = c\left(\frac{t_c}{t_x}\right)^{0.8} \qquad (4)$$

where t_c is the induction period of the control solution; t_x is the induction period of the test solution.

The concentrations of HIO_3 actually used by Landolt and those calculated by means of the above equation are compared in Table 3.

TABLE 3

Accuracy of the Determination of Concentrations of HIO_3

Expt. No.	Molar conc. of HIO_3 taken	Induction period in seconds	Calculated conc. of HIO_3	Relative Error in %
1	3.338	28.36	3.348	+0.20
2	4.450	17.18	4.413	−0.83
3	5.562	12.34	5.542	−0.36
4	6.673	9.08	6.630	−0.64
5	7.783	7.07	7.705	−1.00
6	8.893	5.55	8.906	+0.15

As these results show, the concentrations of HIO_3 calculated by means of the above equation are very close to the actual concentrations of the solution; the relative error varies from +0.3 to −1.0%.

In our experiments we varied the concentration of KIO_3 while keeping the H_2SO_4 concentrations constant at 0.025 M and the Na_2SO_3 constant at 0.01 M.

The values of the induction periods (the reciprocals of the reaction velocity) in the reaction mixtues of KIO_3, Na_2SO_3 and H_2SO_4 for changes of KIO_3 concentration at 20° are given in Table 4.

TABLE 4

Effect of the Concentration of KIO_3 on the Induction Period in Mixtures with Sulfite in the Presence of Acid, at 20°

Expt. No.	Iodate conc. in mole/liter	Induction Period in seconds			
		1	2	3	Mean
1	0.01800	10.5	10.4	10.6	10.5
2	0.01350	14.2	14.2	14.2	14.2
3	0.00900	21.5	21.2	21.2	21.3
4	0.00675	29.5	28.8	29.8	29.7
5	0.00450	46.5	46.6	46.2	46.4

Results for the determination of n necessary for the calculation of the KIO_3 concentrations are given in Table 5.

This table shows that the average value of n at the given temperature is 0.95. Therefore for the solutions of KIO_3 in Table 5 the concentrations can be calculated by means of the equation

$$x = c\left(\frac{t_c}{t_x}\right)^{0.95}. \qquad (5)$$

The results of these calculations are given in Table 6. A KIO_3 solution with concentration 0.018 M was used as the control solution.

TABLE 5

Comparison of Induction Periods for Solutions with Different Concentrations of KIO_3

Expt. No.	Molar concentration of comparable iodate solutions		Induction period for comparable solutions		$n = \frac{\log c_1 - \log c_2}{\log t_2 - \log t_1}$	Mean value of n
	c_1	c_2	t_1	t_2		
1	0.01800	0.01350	10.5	14.2	0.95	
2	0.01800	0.0090	10.5	21.3	0.98	0.95
3	0.01800	0.00675	10.5	29.7	0.94	
4	0.01800	0.00450	10.5	46.2	0.93	

TABLE 6

Accuracy of the Determination of Concentrations of Iodate

Expt. No.	Molar concentration of KIO_3 taken	Induction period in seconds	Calculated molar conc. KIO_3	Relative error, %
1	0.01350	14.2	0.01352	+0.15
2	0.00900	21.3	0.00919	+2.11
3	0.00675	29.7	0.006704	−0.74
4	0.00450	46.4	0.00440	−2.22

TABLE 7

Reaction Velocity of Iodate with Sulfite in Acid Media in Relation to the Sulfite Concentration at 20°

Expt. No.	Concentration of sulfite in mole/liter	Induction period in seconds			
		1	2	3	Mean
1	0.00600	31.2	31.6	31.8	31.5
2	0.04500	35.2	34.8	35.0	35.0
3	0.00300	40.2	40.6	40.0	40.2
4	0.00225	45.2	45.2	44.8	45.1
5	0.00150	52.6	52.0	52.2	52.2

Effect of Sulfite Concentration. A 0.006 M solution of Na_2SO_3 was prepared as the base solution and other solutions of different concentrations prepared from it by dilution.

The concentrations of the H_2SO_4 and KIO_3 solutions were 0.05 and 0.004 M, respectively. The method adopted was as before (equal volumes in a test tube).

The induction periods for different solutions of Na_2SO_3 are given in Table 7, while the respective values of n used in the equation for calculating the Na_2SO_3 concentrations are given in Table 8.

A comparison of the values of n obtained for the Na_2SO_3 solutions shows only a small deviation from the mean value of 2.76.

The concentrations of Na_2SO_3 calculated according to Equation (6) given below, for the solutions prepared by dilution of the Na_2SO_3 control solution, are given in Table 9.

$$x = c\left(\frac{t_c}{t_x}\right)^{2.76} \qquad (6)$$

TABLE 8

Comparison of the Induction Periods for Different Sulfite Concentrations

Expt. No.	Molar conc. of comparable solutions of sulfite		Induction period for comparable sulfite solutions		$n = \frac{\log c_1 - \log c_2}{\log t_2 - \log t_1}$	Mean value of n
	c_1	c_2	t_1	t_2		
1	0.00600	0.00450	31.5	35.0	2.727	
2	0.00600	0.00300	31.5	40.2	2.843	2.76
3	0.00600	0.00225	31.5	45.1	2.732	
4	0.00600	0.00150	31.5	52.2	2.744	

TABLE 9

Accuracy of the Determination of Sulfite Concentrations

Expt. No.	Molar conc. of sulfite taken	Induction period in seconds	Calculated conc. of sulfite	Relative error, %
1	0.00450	35.0	0.004485	−0.33
2	0.00300	40.2	0.003060	+2.00
3	0.00225	45.1	0.002230	−0.89
4	0.00150	52.2	0.001490	−0.67

All these results show that the chronometric method described above can be used to determine the concentrations of iodate and sulfite in their acidified reaction mixtures fairly accurately.

The value of n determined for substitution in the equation for calculating the concentrations of KIO_3 and Na_2SO_3 can of course be changed according to the conditions. The concentration of H_2SO_4, the molar ratio of KIO_3 to Na_2SO_4, and the temperature all affect the value of n. n must therefore be determined independently in each individual case, by using two control solutions of the salt to be determined, the concentration of one of these solutions being twice that of the other.

Let the concentration of control solution 1 be c_1, that of control solution 2 be c_2. Then from Equation (2) the value of n is calculated (see Equation 3). By substituting $c_1/2$ for c_2 we get:

$$n = \frac{\log 2}{\log t_2 - \log t_1} \qquad (7)$$

and

$$n = \frac{0.301}{\log t_2 - \log t_1} \qquad (7a)$$

If the value of n derived from Equation (7a) is substituted in Equation (2) we finally get the equation for calculating the concentration of the salt to be determined.

$$x = c\left(\frac{t_1}{t_x}\right)^{\frac{301}{\log t_2 - \log t_1}} \qquad (8)$$

where c is the concentration of the control solution; t_1 the induction period of the control solution before dilution and t_2 the induction period of the same control solution after dilution with an equal volume of water; t_x the induction period for the test solution.

The methods for the determination of concentration of additives (different salts) will be described in a further communication.

SUMMARY

1. The reaction velocity between KIO_3 and Na_2SO_3 in the presence of H_2SO_4 has been studied with respect to the H_2SO_4 concentration.

2. The effect of the concentrations of KIO_3 and Na_2SO_3 respectively on the induction period of the reaction has been investigated.

3. The analytical significance of this reaction for the chronometric determination of the concentrations of KIO_3 and Na_2SO_3 in their reaction mixtures has been pointed out.

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THE INTERMEDIATE POTENTIAL JUMP DURING THE POTENTIOMETRIC TITRATION OF SOLUTIONS OF ALUMINUM SALTS WITH SODIUM FLUORIDE

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When solutions of aluminum salts are titrated with NaF a small intermediate potential jump is observed after the addition of from $\frac{1}{3}$ to $\frac{1}{2}$ of the equivalent amount of NaF solution. This phenomenon has not been theoretically explained [1]. In the presence of Mg^{2+} this jump is more pronounced. Polyak [2] noticed that if at the point when a potential jump is observed, a few drops of very dilute acid are added, then the former potential is established, while subsequently the potential changes more rapidly in the neighborhood of the equivalence point. We have made it our aim to try and explain this phenomenon.

EXPERIMENTAL

A compensating circuit with a mirror galvonometer was used ($2.4 \cdot 10^{-9}$ Å/mm/M). A platinum ferro-ferri electrode served as the indicator while a saturated calomel electrode was used as the auxiliary electrode.

All the reagents used $KAl(SO_4)_2 \cdot 12H_2O$, NaCl, ethyl alcohol, $FeCl_2$[1)], $FeCl_3$, and quinhydrone were chemically pure. Chemically pure NaF was freed from Na_2SiF_6 by Tananaev's method [3]. Firstly, parallel titrations were made of 4.85 ml of a 0.0332 M solution of $KAl(SO_4)_2$ with 0.1073, 0.2146, 0.4291 M solutions of NaF respectively in an aqueous-alcohol medium saturated with NaCl and with the addition of a small amount of $FeCl_2$ and $FeCl_3$ [1]. The $KAl(SO_4)_2$ was standardized by potentiometric titration with a standard solution of NaF.

TABLE 1

Position of the intermediate potential jump during titrations with NaF. 4.85 ml of 0.0332 M $KAl(SO_4)_2$, and 5 ml C_2H_5OH, 4 g NaCl taken.

Expt. No.	Molarity of NaF solution A	NaF solution used in ml				Ratio $\frac{C}{D}$
		Up to the beginning of the intermediate potential jump B	Up to the end of the intermediate potential jump C	Diff. C − B	For all the titration D	
1	0.1073	2	3	1	8.90	~1/3
2	0.2146	1	1.5	0.5	4.55	~1/3
3	0.4291	0.5	0.8	0.3	2.25	~1/3

Results given in Table and Fig. 1 show that the appearance of the intermediate potential jump corresponds in all cases to the consumption of approximately equal amounts of NaF (ca. $\frac{1}{3}$ of the equivalent wt.).

It is known that in this method [1] the potential jump at the platinum

1) $FeCl_2$ contains some Fe^{3+}.

electrode towards the end of the titration after the quantitative formation of AlF_6^{3-}, is determined by the sharp decrease in the ratio $\frac{[Fe^{3+}]}{[Fe^{2+}]}$ as the result of the formation of FeF_6^{3-}; the latter cannot be formed in the initial stages of the titration when a large amount of the Al is not yet combined. Consequently it is necessary to explain the intermediate potential fall (jump) by some other process, viz. the pH change as shown by a number of experiments. This was confirmed by titrating of the Al salt with a solution of NaF using a quinhydrone electrode (without addition of $FeCl_2$ and $FeCl_3$); in this case also an intermediate potential jump can be observed, which corresponds to the pH[1] change (Fig. 2 and Table 2).

TABLE 2

Change of pH during the titration with the given quinhydrone electrode. 4.85 ml of 0.031 M $KAl(SO_4)_2$, 5 ml of C_2H_5OH, 4 g NaCl taken. Titration carried out with 0.1080 M NaF

Expt. No.	NaF used in ml	E.M.F. in Volts	pH of solution	Conc. of $[H^+]$ in g-ions/liter
1	0	0.2794	2.95	$1.12 \cdot 10^{-3}$
2	0.5	0.2754	3.02	
3	1.0	0.2684	3.13	
4	1.5	0.2594	3.28	$5.25 \cdot 10^{-4}$
5	2.0	0.2374	3.65	
6	2.3	0.2284	3.80	
7	2.6	0.2204	3.94	$1.15 \cdot 10^{-4}$
8	3.0	0.2124	4.07	
9	3.5	0.2064	4.17	
10	4.5	0.1974	4.32	
11	5.5	0.1908	4.43	
12	6.5	0.1804	4.60	
13	7.0	0.1743	4.71	
14	7.5	0.1644	4.87	$1.35 \cdot 10^{-5}$
15	8.0	0.1474	5.16	
16	8.2	0.1414	5.26	
17	8.3	0.1044	5.88	
18	8.4	0.0714	6.43	
19	8.5	0.0567	6.68	$2.09 \cdot 10^{-7}$
20	8.6	0.0479	6.81	
21	8.8	0.0433	6.91	
22	9.3	0.0442	6.84	
23	9.8	0.0397	6.97	

Note: Conc. of $[H^+]$ is assumed to be the same as the activity ($t° = 27.5°$).

Discussion of Results

According to I. V. Tananaev [4] when a solution of NaF is added to the Al salt, a stepwise reaction takes place:

$$Al^{3+} \longrightarrow AlF^{2+} \longrightarrow AlF_2^{+} \longrightarrow AlF_3,$$

or more fully: $AlCl_3 \longrightarrow AlFCl_2 \longrightarrow AlF_2Cl \longrightarrow AlF_3$.

1) The pH value was calculated as usual without taking into account the potential jump on the boundary, water-water alcohol, and the possible effects of Al^{3+} on the quinhydrone.

According to Greenberg [5] AlF_3 is more stable than $AlCl_3$, and simple Coulomb forces play an essential part in the stability of the internal bonds. This fact enables one to calculate approximately the energy of formation (in conventional units [6]) in the series:

$$AlCl_3^{I} - AlFCl_2^{II} - AlF_2Cl^{III} - AlF_3.$$

This calculation confirms the increasing stability of the compounds in the series from $AlCl_3$ to AlF_3 and consequently of a diminishing tendency to hydrolyze. The three stages I, II, III should therefore correspond to the three potential

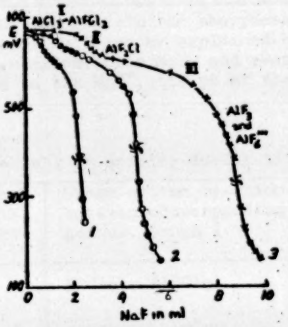

Fig. 1. Titration curves for 4.85 ml of 0.0332 M $KAl(SO_4)_2$ with a ferri-ferro-electrode. 1) 0.429 M; 2) 0.2146 M; 3) 0.1073 M solutions of NaF.

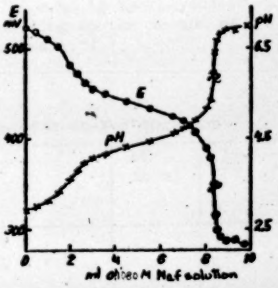

Fig. 2. Titration curve for 4.85 ml of 0.031 M $KAl(SO_4)_2$ with 0.1080 M NaF using a quinhydrone electrode.

drops (acidities), the value of which increases from I to III; this is confirmed by the form of the titration curves (Figs. 1 and 2) and by the experimental results given in Table 3, which were obtained by working out the figures in Table 2. The potential fall in stage I (total final product $AlFCl_2$) cannot be sharp, because it is smoothed out by hydrolysis of $AlFCl_2$; the potential fall in stage II (final product AlF_2Cl) is steeper because it is not smoothed out to such an extent by the hydrolysis of AlF_2Cl (this hydrolyzes less easily than $AlFCl_2$); the potential fall in the final stage, stage III (final product AlF_3 and Na_3AlF_6) is the most significant because there is practically no Al compound left, the hydrolysis of which could to some extent hinder the fall of acidity of the solution.[1] The large section (almost horizontal) of the curve at stage III is explained by the total formation of AlF_3 and Na_3AlF_6.

The amount of NaF which corresponds to the intermediate potential jump is approximately $\frac{1}{3}$ of the equivalent amount of NaF, and corresponds to the formation of AlF_2^+ (stage II) as a stage in the total reaction:

$$Al^{3+} + 6F^- \longrightarrow AlF_6^{3-}$$ [1]

($\frac{2}{6} = \frac{1}{3}$)[2]

In this way the intermediate potential jump (or fall) during titration of

[1] Of course in the presence of Fe^{3+} and Fe^{2+} the potential should drop sharply as the result of the formation of FeF_6^{3-}.
[2] As suggested by Kh. B. Medinsky.

solutions of Al salts with NaF is explained by the exhaustion of all the $AlFCl_2$ (AlF^{2+} and $AlFCl^+$ ions) and the quantitative formation of AlF_2Cl (AlF_2^+ ions). This enables one to explain Polyak's observation [2] that the addition of a small amount of acid at the moment when the potential jump is observed, compensates the lowering of acidity at this point, i.e. increases the potential of the platinum electrode. In view of this, the formation of AlF_3^{3-} also proceeds at a higher potential, while the jump $\frac{\Delta E}{\Delta V}$ becomes sharper, because there is a smaller amount of acid present to hinder the hydrolysis of $FeCl_3$ and at the same time increases the concentration of Fe^{3+}, which determines the sharper final potential jump.

The increase in the sharpness of the intermediate potential jump in the presence of Mg^{2+} can be explained by the fact that $MgCl_2$, e.g., is hydrolyzed to a greater extent than MgF_2 and even MgFCl, so that according to the amount of F^- added to the Mg^{2+}, the pH of the solution should increase.[1])

TABLE 3

Relative fall in acidity during titration of $KAl(SO_4)_2$ with an NaF solution

Index Nos. of points from Table 2	Stage of the reaction between corresponding points. Graph 1	$\frac{c_{H_a^+}}{c_{H_b^+}} = 1$	∂V in ml	$\frac{1}{\partial V}$
1-4	$AlCl_3 - AlFCl_2$	$\frac{c_{H_1^+}}{c_{H_4^+}} = \frac{1.12\cdot10^{-3}}{5.25\cdot10^{-4}} = 2.1$	1.5	1.5
4-7	$AlFCl_2 - AlF_2Cl$	$\frac{c_{H_4^+}}{c_{H_7^+}} = \frac{5.25\cdot10^{-4}}{1.15\cdot10^{-4}} = 4.6$	1.1	4.1
14-19	$AlF_2Cl - AlF_3$	$\frac{c_{H_{14}^+}}{c_{H_{19}^+}} = \frac{1.35\cdot10^{-5}}{2.09\cdot10^{-7}} = 64.3$	1	64.3

Note. $c_{H_a^+}$ and $c_{H_b^+}$ are concentrations corresponding to the points on Graph 1; ∂V is the amount in ml of fluoride solution added in the interval between points on Graph 1.

The practical significance of this intermediate potential jump is that its appearance enables one to foresee the position of the final titration end point, and in rapid analysis to determine approximately the amount of aluminum.

SUMMARY

1. It has been shown that the form of the curve obtained by titrating Al salts with NaF using a ferri-ferro electrode is determined by the potential fall in the platinum electrode as a result of an increase in pH and a decrease of the ratio $[Fe^{3+}]/[Fe^{2+}]$ in solution.

2. A theoretical explanation is advanced for the titration curve on the basis of the increase in stability of the compounds in the following series in going from left to right: $AlCl_3 \longrightarrow AlFCl_2 \longrightarrow AlFe_2Cl \longrightarrow AlF_3$.

3. It has been shown that the intermediate potential jump (fall) is explained by the formation of AlF_2Cl (AlF_2^+ ions), whereby the acidity of the solution decreases, giving rise to a potential fall on the platinum electrode.

[1]) pH ~ 0.1 M $MgCl_2$ < 7 [7] pH of saturated MgF_2 (0.013 g/100 g solution) > 7 [8].

4. It was found that the position of the intermediate potential jump on the titration curve enables the position of the final end point to be forecast when solutions of Al salts are titrated with NaF. In rapid analysis therefore the amount of Al can be estimated approximately by titrating only as far as the potential jump, thereby decreasing the titration time.

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A NEW METHOD OF CONSTRUCTING A BLACKENING CURVE AND ITS USE IN X-RAY CHEMICAL ANALYSIS

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Quantitative X-ray spectral analysis using photographic registration assumes a knowledge of the blackening curve,[1] which have been constructed either by one of the methods described in standard text books [1,2] or by the method worked out recently by Protopov [3]. In the present communication a new method is described for constructing a blackening curve, which differs from the others in its simplicity and its convenience for use in quantitative X-ray spectral analysis. Work carried out in our laboratory showed that by means of this method analyses could be carried out more rapidly and with greater accuracy. The basic idea is as follows. Any method of constructing a blackening curve is based on the comparison of two series of numbers; one characterizing the laws of the changes in intensity of the spectral lines and the other composed of the values for blackening which correspond to each of the points of the first series. The only essential difference between the other methods used hitherto for constructing blackening curves is in the manner in which the investigator interprets the law of intensity changes for the lines used in constructing the curve. In some cases this is achieved by regular weakening of the initial intensity of the lines by means of a special wedge absorber, while in others the intensity of the lines are left unchanged and "intensity marks" are superimposed on the spectrogram by varying the time for which the points on the spectrogram are illuminated.

In the method described here it is proposed to use as the initial intensity series, values which correspond to individual points on the contours of the X-ray spectral lines, particularly those which are symmetrical, and can be described by a dispersion formula. Such lines [5] e.g. are the $K_{\alpha 1,2}$ doublets of practically all the elements the atomic numbers of which, Z, are greater than 30.

The intensity of separate points within the limits of the contours of each of these lines is related to the width of the lines at a given cross section by the simple equation [5]:

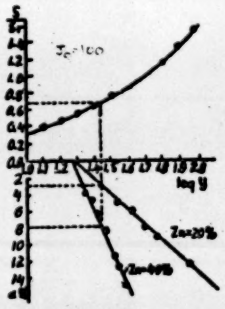
$$x = \Gamma \sqrt{n - 1} \qquad (1)$$

where n is the ratio of the intensity of the line at its maximum to the value at some arbitrary point on the contour; x is the width of the line at this cross section and Γ is the so-called half width. The applicability of (1) to different classes of X-ray spectral lines was verified experimentally and was used for studying the form of the $K_{\alpha 1,2}$ doublets of different elements forming components of chemical compounds and alloys [5]. It, i.e. (1), can be used for solving the

[1] In those cases [4] where construction of the blackening curve in an explicit manner is essential for carrying out analyses, it is necessary to use a number of coefficients obtained empirically, the relation of which to the content of the element to be analyzed is determined by the absence of proportionality between the blackening of the lines on the spectrogram and their intensity.

problems which are the subjects of the present communication. For this purpose we consider those changes in the form of the symmetrical X-ray spectral line which occur during its registration on the X-ray plate. To each point of the original contour mapped out on the intensity scale there will correspond a definite point on the experimentally registered (on the blackening scale) profile of the spectral line. One curve is transformed into the other. The law which governs this transformation is the required relation between blackening and intensity. It is different for different types of photographic material. In practice, however the possibility of a reverse transformation from the known form of the line on the blackening scale to its contour on the intensity scale is important. Such a transformation can be easily realized, if it is taken into account that independently of the concrete form of the law of transformation of one curve into the other[1], two symmetrical points on both curves (corresponding to one value of the blackening or intensity) should remain equidistant. This enables one, having measured the width of the line at any given section of the experimental profile (on the blackening scale), by means of equation (1) to find the value n on the true profile of the line (on the intensity scale) which corresponds to a given value of the blackening.

In order to do this only the value of Γ relating to the true profile of the spectral line is necessary.



In the simplest case, when the spindoublet is used for the construction of the blackening curve, the value of Γ can be easily determined. In view of what was stated above it should be equal to the width of the experimental line $K\alpha_1$, measured for a blackening value on its profile, which is equal to the value of the blackening at the maximum for line $K\alpha_2$. The intensity of the latter line is known to be approximately equal to half of the intensity of $K\alpha_1$ and does not depend on the experimental conditions.

In the general case when the singlet lines are used, the experimental determination of Γ can be carried out by means of measurements made on lines, a part of the length of which is artificially weakened by absorption in an aluminum foil of an arbitrary but known thickness.

Thus, to each arbitrarily selected value of blackening on the experimental profile of $K\alpha_1$ lines it is possible to assign a corresponding intensity value, expressed on an arbitrary scale, which corresponds to the intensity of the line at its maximum (I_0). This is the required relation $S = S(I)$; its form should not depend on the chemical nature of the element, the $K\alpha_{1,2}$ line of which is selected for constructing the curve[2] for the compound into whose composition the element enters[3]. Its form should also be independent of the apparatus used.

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1) In other words independently of the concrete form of the required relation $S = S(J)$.
2) If the relation between the photoactivity of the X-rays and the wave length of the radiation is not considered.
3) If the symmetry of the $K\alpha_{1,2}$ line is not destroyed.

In order to use the blackening curve constructed by the method described above it is convenient, however to transform it into a form which is independent of the selection of the values for the initial intensity – I_0. This can be accomplished, if instead of the curve $S = S(I)$ a curve is constructed of log I against the ratio of the blackening of an arbitrary point on the experimental profile of the $K\alpha_1$ line to the blackening of the $K\alpha_2$ line at a point corresponding to its maximum. Both these values are determined by taking into account the background of the spectrogram. A curve of this type which was obtained for a Mark XX plate is represented in the figure (upper portion). It was constructed on the basis of a large number of independent points obtained by the use of the $K\alpha_{1,2}$ doublets of Cu and Zn, taken with a Johann-Koshu spectrograph.

By means of the curves given in the diagram it is possible to get highly accurate analyses within the range of ratios of S/S_r from 0.3 to 1.3. The amount of the element used for comparison in the sample ignited should be chosen (as shown experimentally) so that the blackening of the $K\alpha_2$ line appears to lie within the limits 0.2 to 0.75. When this is done the deviation of the experimental points from the curve represented in the diagram is negligible. Outside the range for S/S_r given above, the extent of the agreement between the experimental values of J/J_0 and the values determined from the curve decreases and appears to be dependent on S_r.

On the lower part of the diagram graduation curves are represented which were obtained by means of two series of specially prepared synthetic mixtures, in which the content of the element to be determined was varied while the content of Zn (the element used for comparison) was kept constant at 20% and 40% respectively. Comparison of the upper and lower curves enables an analysis to be carried out with an accuracy of not less than 4-6% of the actual amount. This is done by measuring the blackening of the corresponding lines of the element to be analyzed and the blackening of the maximum of the $K\alpha_2$ line of the comparison element. The results and accuracy of the analyses when this method is adopted are practically independent of the variation in exposure time and the working condition of the spectrograph tube, and also of the variations in the background of the spectrogram. There is no need for any special conditions for developing the spectrograms. At the same time, the fact that within the wide concentration range of the element to be analyzed in the test sample, the content of the comparison element can remain strictly constant, enables one automatically to take into account the change in the conditions for applying the substance to be analyzed to the surface of the anticathode of the X-ray tube, and to reduce to a minimum the detrimental effect of this factor on the accuracy of the analyses. Thus the comparison element used in our experiments also plays the part of a "fixing element" so that differences in the conditions used for excitation of the X-rays in test samples which cover the surface of the focussing spot of the X-ray tube differently, need not be taken into account.

In conclusion it can be stated that the method described above[1] for constructing a blackening curve can be used for quantitative analyses and can be applied in X-ray structural analyses and in optical and other fields of investigation.

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1) After some minor modifications.

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A DISMOUNTABLE X-RAY TUBE WITH A REVERSE RAY PATH FOR X-RAY SPECTRAL ANALYSIS

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Despite the numerous merits of the X-ray spectral method of analysis, as far as its sensitivity is concerned it cannot compete with optical methods in the majority of cases. One of the main factors which lowers the sensitivity of X-ray chemical analysis is the continuous spectrum; its presence on the spectrogram during analysis of samples containing small amounts of the element to be determined often makes it impossible to distinguish the lines of the characteristic spectrum on such a background. One of the methods therefore of increasing the sensitivity of the X-ray method is to weaken the continuous background as much as possible.

The most radical method of solving the problem, whereby, at least in theory the background of the spectrogram which is determined by the continuous spectrum can be almost completely eliminated, was that proposed in 1936 by Blokhin [1] and after 11 years "rediscovered" by Holubei and Cauchois [2]. This method is based on the fact that in contrast to the characteristic X-ray radiation which is propagated in all direction with equal intensity, the continuous spectrum which interferes in X-ray chemical analyses is polarized. It has, as many investigators have shown, a minimum intensity in the direction of the retardation of the cathode beam which excites the X-rays and amounts to not more than 15% of the intensity of the radiation, measured in a perpendiculer direction. Therefore if the X-rays are directed from the tube in the direction of impact of the cathode electrode beam, then theoretically it should be possible to separate almost completely the characteristic spectrum from the continuous one.

In spite of the undoubted merits of the idea mentioned above, hitherto not only has no reliable apparatus based on this idea been constructed or the idea accepted in practice by investigators in this field, but it has not even been reliably tested experimentally (as far as can be judged from literature sources). We are aware that the tube constructed by Blokhin is not irreproachable.

It seemed expedient therefore to construct an experimental model with a reverse ray path and to study its merits and demerits for carrying out X-ray chemical analyses (vide Fig. 1).

The tube is mounted on the base of an RSK-1 X-ray spectrograph. The casing is a rectangular brass block with openings for anticathode, high vacuum pump and an LT-2 for measuring the vacuum and a slit for emmission of the X-rays. The anticathode was fixed on a porcelain insulator with four screw clamps. The insulator on the conical section fixes into the tube casing. The cathode is prepared in the form of a rectangular cover in which a slit is cut, covered with an aluminum foil 20 μ thick. The foil which separates the internal part of the tube from the atmosphere is clamped to the cathode by means of a special lamina fitted with a thin lead gasket. The cathode is clamped with four bolts fitted with rubber gaskets to the tube casing, while the filament with focussing flanges fixes into the slit of the tube casing. A straight platinum wire 0.3 mm in diameter and 45 mm long was covered with strontium oxide. By using conical sections and threaded

spindles on which the filament with focussing flanges is mounted, the distance from anticathode to filament can be changed under high vacuum from 15-35 mm. The tube operates at its optimum when the distance between cathode and anticathode is kept within the limits of 17-20 mm. The cathode and the tube casing were not cooled artifically, because although the tube was operated for 2 hours at 45 kV and 20 mA, the apparatus only heated up to 5-10° more than the surroundings.

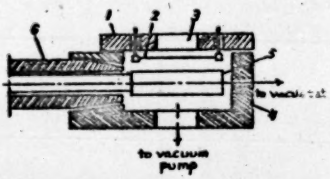

Fig. 1. Schematic features of the X-ray tube with reverse ray path. 1) cathode, 2) filament, 3) slit for the X-rays, 4) tube casing, 5) anticathode, 6) porcelain insulator.

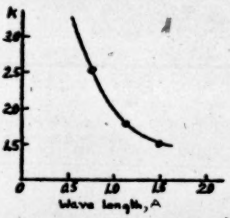

Fig. 2 Relation between the coefficient K and wave length.

After constructing the tube with a reverse ray path its performance was compared with that of a tube of normal construction. In order to do this, spectrograms were taken using an RSK-1 apparatus with the normal X-ray tube in addition to spectrograms taken with the new tube. The working ranges of both tubes were the same 45 kV at 20 mA. The exposure time was varied from 5-120 minutes. A quartz plate cut along the surface $(10\bar{1}0)$ and bent along a 100 cm radius was used as the reflecting surface. The value of the working part of the crystal was 4 mm in all cases. The focussing spot on both apparatuses was 20-24 mm long and 5-6 mm wide. The test mixture, prepared by chemical methods and containing oxides of Ta, Nb, As and Sn, was smeared on the rifled cathode surface. The radiation was registered by means of a two sided X-ray plate – XX (Russian make). Photometric measurements of the plate were made with a visual MF-2 photometer. The integral intensity of the lines was measured.

The $K_{\alpha_{1,2}}$ doublets of As and Nb for two orders of reflections were chosen as the supporting lines for the comparative study of the two X-ray tubes. The ratio of the blackening of the line of the characteristic spectrum to the blackening of the continuous background in the wave length range from 740 to 1490 Kh.E. that corresponds to Woolf-Bragg angles of 5-10°.

Average results for test runs of the two tubes are given in the table below. This table also includes values of the coefficient K, which characterizes the ratio of blackening of the comparison lines obtained with the two tubes to one value of the background.

Fig. 2 shows clearly that the tube with the reverse ray path is most effective in the short wave and low reflection angle region.

In spite of the limiting simplicity of construction of the experimental model described here with a reverse ray path and the snags associated with such a construction, its results are promising. We feel confident that the construction

of a more powerful and better constructed tube and the subsequent use of such an improved model in X-ray technique [3] should demonstrate the merits of this method for increasing the sensitivity of the X-ray method to greater advantage.

Element	Order of reflection	Si/Sf		K
		Normal tube	Tube with reverse ray path	
NbK_{α_1}	I	2.21	5.67	2.56
AsK_{α_1}	II	6.97	12.59	1.80
NbK_{α_1}	II	3.01	4.67	1.54

In conclusion I should like to express my thanks to E. E. Vainshtein for proposing this scheme of work and for his help in its fulfillment.

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NEW APPARATUS FOR ELECTROCHEMICAL METHODS OF ANALYSIS

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A Streaming Mercury Cathode

Mercury cathodes in the form of a jet are used for preparative purposes in electrochemistry, for preparing metal amalgams [1] for the electro-reduction of organic compounds [2], for studying the mechanism of cation discharge [3] and in oscillographic polarography [4].

The set-up which we have constructed, which includes a streaming mercury cathode, is depicted in Fig. 1. Chemically pure mercury is contained on the bottoms of the three connected vessels 1,2 and 3.[1] II is connected via a tap 10 to 9; 9 can be evacuated by means of a water jet pump, connected to tube 5. Mercury from the

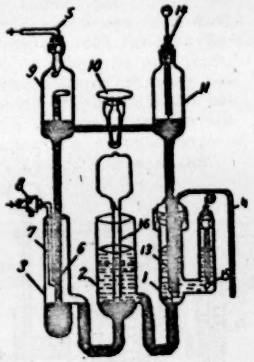

Fig. 1. Set up for streaming mercury cathode. 1) electrolyzer; 2) partition for decomposition of the amalgam; 3) mercury receiver; 6) tube for leading mercury into 9; 7) T-piece with valve 8 for leading in nitrogen; 5) connecting tube to water pump; 10) tap; 11) bulb for passing mercury to the electrolyzer; 13) capillary tube; 15) anode; 4) electrolytic switch for electrode comparison.

bottom of 3 rises in tube 6 up to the T-piece junction at 7. By the action of a stream of nitrogen, sucked through valve 8, the mercury column in tube 6 breaks up into separate parts and is sucked into 9. After filling 9 with sufficient mercury, the vacuum is switched off and tap 10 is opened; the mercury flows in 11 and from there along capillary tube 13 in a jet into 2 (the electrolyzer).

The set-up subsequently works automatically by switching on the vacuum. The amalgam formed by cathodic polarization of the mercury jet flows from 1 into 2, where it is decomposed by means of acid and is mechanically stirred with a glass stirrer 16. The mercury goes from 2 to 3, from which it again rises into 9, etc.

Thus in the apparatus described the same mercury is used over and over again for obtaining a continuous jet of mercury, which serves as a cathode for an indefinite time.

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[1] For methods of purifying mercury see [5].

The negative pole of the current supply source is connected to the platinum contact 14, while the platinum anode is fixed in the side tube 15. The potential of the streaming cathode is measured during polarization by reference to a saturated calomel electrode by the usual compensating system. The distance of the end of the electrolytic switch from the mercury surface is fixed because the switch and the capillary tube 13 are fused into the cover.

Fig. 2 Restriction of the lower end of the jet.

It was observed that with increasing current density the jet does not remain constant but increases. Under the action of the current the jet breaks up into small drops, the place at which the break up occurs however cannot be established even under strong magnification. In some essential cases (e.g. for calculating current density) the lower end of the jet can be confined with the help of a little shaft, fused into the cell wall (Fig.2)[1].

An Apparatus with a Renewable Flat Cathode

Of all the apparatuses described hitherto which have a renewable mercury cathode [5,8], the Hildebrand cell is the most often used in electroanalysis [9]. We found that during the electrolysis of weak solutions of metals which can form amalgams, this apparatus does not always ensure good results in the sense that the separation of the metal is complete and pure. This can be explained by a) an insufficiently intense exchange of mercury between the two separation cells, which leads to a change in the deposition potential of the metal as the result of an increase in its concentration in the amalgam located in the cathode compartment; b) the penetration of undecomposed electrolyte into the compartment used for the decomposition of the amalgam.

These drawbacks have been eliminated in the apparatus depicted in Fig. 3. The mercury is located at the bottom of the two vessels 1,2 which are doubly connected, 2 serves as the electrolyzer in which the mercury on the bottom serves as a cathode; the anode is separated from the catholyte by a porous diaphragm 5. When the stirrer 6 in the form of a corkscrew is rotated, the mercury in tube 7 is pumped up into 1, in which its level becomes higher than that in 2, so that there is a flow from 1 into 2 via 8. The renewal of the cathode surface in 2 is also assisted by stirrer 9 driven by the motor 12 by a pulley attachment. The length of the vertical parts of tubes 7 and 8 is sufficient to hinder the penetration of the electrolyte from 2 into 1, where the amalgam is decomposed. The decomposition velocity of the amalgam can be increased by anodic polarization from an independent D.C. supply (e.g. a dry 1.5-2 volt battery); a platinum-tin electrode immersed in the electrolyte in 1 serves as the cathode in this case.

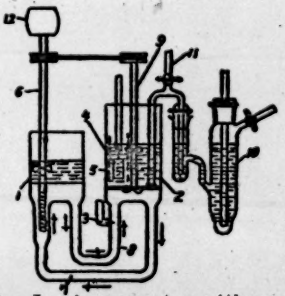

Fig. 3. An apparatus with a renewable flat cathode. 2) electrolyzer; 3) platinum contact; 4) anode; 5) porous diaphragm; 1) compartment for decomposition of amalgam; 6) corkscrew stirrer; 7-8) tubes for mercury flow and amalgam; 9) glass stirrer; 11) electrolytic switch; 10) standard electrode; 12-motor.

1) The streaming mercury cathode has the following advantages over a flat cathode a) the possibility of polarizing with a large current strength without appreciable heating of the solution as a result of Joule heating; b) lower concentration polarization because of the vigorous stirring of the solution by the mercury jet [7].

The cathode potential is standardized against an electrode suitable for any particular set of experimental conditions. A suitable form is shown in Fig. 3.

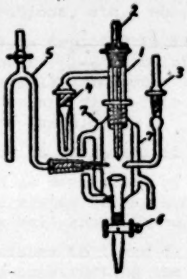

Fig. 4. Cell for polarographic analysis. 1) tube on a rod for strengthening the capillary electrode, 2,3,4) inlet and outlet tubes for hydrogen; 5) electrolytic switch; 6) outlet tap for mercury; 7) water jacket

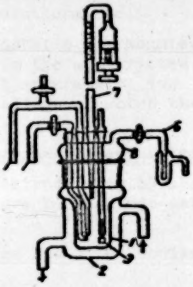

Fig. 5. Cell for potentiometric titration. 1) working volume (constricted part); 2) water jacket; 8) ground glass cover with tubes; 4,6 inlet and outlet tubes for nitrogen; 3) reference electrode; 5) electrolytic switch; 7) microburette.

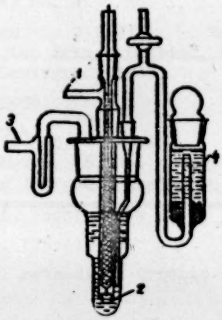

Fig. 6. A cell for pH determination by means of a hydrogen electrode. 1,3) inlet and outlet tubes for hydrogen; 2) platinum electrode; 4) saturated calomel electrode

Apparatus for Polarographic and Potentiometric Analysis 1 ..

a) A cell is shown in Fig. 4 which can be used for polarographic analyses with both external and internal anodes. In the latter case the potential of the mercury drop is measured by reference to a saturated calomel (or some other reference electrode) by means of the electrolytic switch 5. Capillary 2 is fixed on to a rubber cork, which is separated adequately from the solution in the cell. This separation is important in order to avoid contamination of the solution and deformation of the polarograph wave by the action of surface active materials [10]. The cell is thermostated by means of a jacket fused on to it, through which water heated to the required temperature in a Heppler thermostat is circulated.

b) Normally for potentiometric titration in an inert atmosphere all the details are mounted on the cork on a support [11]. Such a method is extremely inconvenient, particularly when working with very small volumes of solution, since it leads to accidents to some of the parts, and also to contamination from rubber connections, etc., when working with heated solutions, etc.

An apparatus is depicted in Fig. 5 in which all the details are mounted on a ground glass cover. 1-2 ml solution can be dealt with in the constricted lower part of the cell. In order to measure the potential accurately, two platinum electrodes are fixed into the cover, from the readings of which the average values are taken.

The apparatus is thermostated in the same way as described in apparatus (a).

c) When a pH is determined by means of a hydrogen electrode (Fig.6) there is no need to thermostat the apparatus since the temperature corrections can be calculated from a well known formula [12].

The author wishes to thank G. S. Tyurikov, P. N. Palei and I. A. Novikov for their help in constructing the apparatus.

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OBITUARY

VASILY IVANOVICH LISITSYN

(1886-1952)

Vasily Ivanovich Lisitsyn, an analytical chemist who was manager of the Chemico-Analytical Laboratory of the All Union Institute of Mineral Raw Materials and a director of the Geological Service, died on the 2nd of February after a long and grievous illness.

The Institute has lost a warm personality as well as an outstanding specialist in V. I. Lisitsyn, while the Chemical Society of the Union has lost a talented man who always helped those who turned to him for assistance.

V. I. Lisitsyn was born in 1886 of a peasant family. After completing a course at the Classical Gymnasium in 1903 he went to Moscow University.

He was arrested in 1906 for his revolutionary activities and sentenced to eight months in jail. In spite of this he finished his course in the natural physico-mathematical faculty of the University with honors; his outstanding capabilities were recognized by his Professor so that on graduating he was asked to remain at the University in N. D. Zelinsky's department. However the Trustees of the Moscow Scholastic circles refused his candidature because of his political unreliability.

V. I. Lisitsyn began his working life in various laboratories in Moscow, Leningrad and the provinces. Tuberculosis of the lungs, however, compelled him in 1918 to return to his native village where he led an agricultural artel until 1930.

When his health had improved, Lisitsyn entered the chemistry laboratory of the All Union Institute of Mineral Raw Materials (then the Institute of Applied Mineralogy) in 1930. After accepting the leadership of this laboratory in 1931, he remained there till his death.

In the course of his 22 years work at this Institute he showed superior capacities as a talented investigator and organizer.

The laboratory in his charge is rightly regarded as one of the best analytical laboratories in our country. In this laboratory the most important umpire analyses have been carried out. The laboratory fulfilled a large amount of work on the preparation of standard samples, and completed considerable research work, side by side with a vast amount of industrial analyses. In this laboratory, where Lisitsyn could combine both research and industrial collectives, more than 50 elements were determined.

Lisitsyn developed exceptional conditions for scientific research work, and for the training of scientific cadres. His co-workers in the laboratory published numerous papers in scientific literature and developed a large number of various analytical methods. Many of his co-workers completed and defended their theses, and several of them subsequently became doctors of science and professors.

In a review article devoted to the achievements of Soviet Science for the last 30 years, the laboratory led by Lisitsyn was numbered as one of the "outstanding schools of analytical chemistry in our country, a center of scientific

thought on analytical chemistry" (J. Appl. Chem. 20, 1045 (1947).

The most noteworthy characteristic of Lisitsyn's activity was his unceasing care for the development of laboratories of the peripheral geological administrations, and the training of cadres of young specialists in these laboratories.

Workers in the furthest laboratories of the geological administrations and on expeditions who turned to Lisitsyn always received the closest attention to all their questions, together with exhaustive consultations and comradely support. His faultless work over many years in the service of our Socialist country was highly valued by the Government. He received Government awards and thanks.

In V. I. Lisitsyn we have lost a warm personality, a talented analyst, and a considerate and skillful leader.

Everyone who met Lisitsyn while he was alive will cherish his memory.

CRITICISM AND BIBLIOGRAPHY

Yu. S. Lyalikov. "Physico-Chemical Methods of Analyses" (A Textbook for Metallurgical Students and for Students of Coke Chemistry) 2nd edition, revised and enlarged. Met. Press. Moscow, 1951, 308 pp. with illustrations. 10 roubles 95 kopecks

The appearance of a 2nd edition of Lyalikov's textbook is proof of its merits and the need for this book, in which all the more or less widely known and often used physico-chemical methods of analyses are set out in an accessible form. Although the book is designed as a textbook for metallurgical and coke-chemistry technical schools, it can, for lack of a more fundamental textbook, serve as a hand book for workers in factory laboratories and for students in chemistry colleges.

Yu. S. Lyalikov, having taken into consideration all the observations and wishes regarding the 1st edition, has subjected his book to a fundamental revision which has enhanced its value considerably. It is particularly consoling to observe that in a new chapter the author has given a fairly detailed treatment of the part played by our country's scientists in the development of physico-chemical methods of analyses and has corrected historical errors in relation to the contribution of Russian and Soviet scientists in this field.

In this new edition, the chapter devoted to spectroscopic analyses has been left out without sufficient reason. If the aim of this textbook is to acquaint students with fundamental physico-chemical methods, then the author should either thoroughly correct and remodel the chapter indicated, or hand it over to a competent specialist. A reference to the effect that there are already in existence or that there are specialist textbooks in preparation on spectroscopy is unconvincing. Other chapters could be included with equal success. Meanwhile spectroscopy, as one of the most important and valuable physico-chemical methods of analyses, should find its rightful place in any textbook devoted to the field of analytical chemistry.

At the end of each of the eleven chapters, problems and questions are included which facilitate the utilization of the material set out.

General information and the principles of mathematical and graphical treatment of results of observation are set out in the 1st chapter. The description of the graphical treatment of results is somewhat shorter than in the 1st edition. This cannot be justified, because of its importance to students.

The second chapter is devoted to visual colorimetry. The material is set out exhaustively in a manner readily accessible to the beginner. Both theoretical and practical questions are treated well. The method of describing the apparatus, its use, and the selection of practical work is very successful. Unfortunately the author continues in this new edition to switch his terms in an arbitrary fashion; e.g. light strength, amount of light, intensity of light, light value, etc.

The theoretical basis and practice of nephelometric analysis is given in Chapter IV. There are no essential drawbacks. It is incomprehensible, however, how in § 2 in the description for converting the normal colorimeter into a nephelometer, it is possible to observe by means of an eye piece a light beam

scattered by particles, when the author recommends that the immerser be covered with a black lacquer. He probably means that only the side walls of the immerser should be covered and not the lower surface.

Chapter IV is devoted to a rather full discussion of the theoretical basis, the apparatus, and the technique of photocolorimetry in a way that indicates a good knowledge of the material.

There are a few inaccuracies and unclear formulations, e.g. on p. 273 it is stated that on applying a certain potential to two plates fixed in a vacuum, a current does not flow in the circuit because electrons do not traverse a vacuum, and further on, illuminating the cathode, electrons break away which proceed to the anode and a current flows in the circuit. It is pertinent to speculate on the manner in which the electrons move in a vacuum in the 2nd instance, if as the author affirms earlier, they cannot traverse a vacuum. On p. 78 it is stated re the photoelement with an internal photoeffect: "if a certain potential difference is preliminarily applied to the electrode" while the author has in mind the application of the potential difference to the two electrodes. The application and selection of light filters is not successfully explained (pp 86-87). It would not be amiss to give a definition of lumen. Here again we meet with the parallel use by the author of the term intensity and strength of light for one and the same phenomenon. The mathematical relation between the voltage applied to the light source and the strength of the light flow is not completely accurately formulated on p. 90. This definition does not correspond fully with the graphical representation of this relation given there. On p. 100 in a description of the preparation of solutions for constructing a calibration curve, the author having dissolved 0.1 g of steel succeeds somehow or other in adding to one and the same solution 2.5, 5, 7.5... 25 ml of a standard solution of Ni, and prepares a series of solutions with different concentrations of Ni! There are also errors in answers to problems, e.g., p. 102, problem 2, etc.

In Chapter V the author deals with the refractometric method of analysis. The amount of information given corresponds to the practical importance of the method. The most widely used apparatus in laboratory practice has been picked out, together with theoretical information, and examples are given for practical work with the apparatus described.

The derivation of refractive index and the formulation of this concept is not clearly expounded. The author correctly defines the refractive index as the ratio of the sine of the incident angle to the angle of refraction for light passing from one medium into another. Further on however he states "when a ray of light passes from a more refracting medium into a vacuum or into air, for which the refractive index is equal to unity etc.", of course one medium on itsown cannot possess a refractive index. Similarly the refractive index in formula (2) cannot be deduced from equation (1) p. 105, when sine β is equal to unity. It is not indicated in Table 12 what media the refractive indices of the tabulated substances refer to.

The polarometric method is discussed in chapter VI. The principle of the method is briefly described, together with the fundamental apparatus and technique. Unfortunately on p. 125, where the equation relating the specific rotation of the plane of polarization is given, it is not clear whether the sign denotes a minus or a hyphen. On Fig. 86 the ratio between d_1 and d_n is wrongly expressed. On Fig. 89 the column 16 is not marked etc.

Electroanalysis is considered in chapter VII which is one of the most reliable ones. Although considerable space is devoted to electrolysis, the exposition is not always clear and systematic, and in some instances suffers from simplification, e.g. in the explanation of the origin of electrode potentials, chemical polarization, etc. One of the drawbacks of this chapter is

the discussion of all the theoretical bases of electrolysis in only 24 pages, in which are included discussion of normal electrolysis, internal electrolysis, overvoltage, polarization, and practical questions, without any indication of the relations between them. The way in which this chapter has been compiled hinders reading and use of the material.

Apparatus, technique and practical problems are described thoroughly. Errors noted here are as follows. The way in which the equation of the discharge of PbO_3^{2-} to give PbO_2 on p. 153 gives rise to doubts as to whether it is the ion $Pb^{4+}O^{2-}$ or the molecule PbO_2. There is no congruence between a statement in the textbook (p. 157) to the effect that in a neutral medium $E_{Ni} < E_{Cu}$ and $E_{Ni} > E_{Zn}$ and the results adduced in Table 19. On p. 171, § 4 as the first practical problem it is suggested that Cu and Sn can be determined by electrolysis, when in fact it should be Pb and Cu.

The student will find the necessary information in chapter VII for learning the principles of conductometric analysis. It is described concisely and clearly. The lamp methods described are not quite so accessible.

Potentiometric methods are the subject of chapter IX – it occupies most space in the book despite the fact that the basic question of the origin of electrode potentials has already been discussed in the chapter on electroanalysis. Here additional information is given on the development of the oxidation-reduction potential, without a discussion of the mechanism of the origin of these potentials. All the four types of reactions which are used in potentiometric analysis are considered. The theoretical and practical material presented in this chapter is fairly comprehensive. Different types of electrodes are described, together with experimental set ups and apparatus for titration. Unfortunately, the author has nothing to say about potentiometers, either lamp types or simple ones, as issued by the MOSKIP factory. This observation applies equally to photocolorimeters – mark FEK-M, MOSKIP, etc. Young students should be made aware of Russian apparatus which is available.

Chapter IX contains the greatest number of mistakes, misprints, innaccuracies and nebulous formulations, e.g. in the formula for potentials of systems, although factors which are responsible for deviations from normal potentials are indicated, the reasons for these deviations are not discussed. The derivation of the potential at the equivalence point is not well put. It is not at all clear what the author means by the initial concentrations of the reaction products. The statement that the equilibrium potential of an oxidation-reduction system is defined as the average arithmetic oxidation-reduction potential of the system participating is incorrect. The choice of the term "antimony oxide electrode" is an unfortunate one, since it has been customary to use the term "antimony electrode" for a long time. On p. 212, in calculating the titration potentials of silver cyanide, the minus sign is continuously omitted. On p. 154, the level of the liquid in the hydrogen electrode is incorrect. In Table 28 it is correctly stated that the potential of the antimony electrode depends on the method of preparation; but for the glass electrode a mathematical relation is given between potential and hydrogen ion concentration. Maybe the potential of the glass electrode is a constant for all cases and is independent of the method of manufacture and the composition of the glass!! It is incomprehensible how a reverse titration of Co^{2+}, Ni^{2+}, Zn^{2+} (Table 29) can be carried out, by means of a silver electrode, with $AgNO_3$ as the working solution. In the graph of the exchange potentials, normal potentials of the systems are given; these concepts are heterodynamic. Further it is not clear how it is possible to titrate pentavalent vanadium with permanganate, cerium sulfate (IV) and chromium sulfate (II). Incidentally the ion V^{5+} does not exist. The same can be said about the impossibility of titrating

iodides, $Ce(SO_4)_2$-iodates, $CrSO_4$- bivalent Fe, etc., with $TiCl_3$. Such misprints are inadmissible in a textbook. A method for non-compensated titration up to the point when there is no current in the system, is incorrectly described, because nothing is said about the choice of suitable reference electrodes for each individual case.

In the section devoted to practical work, mistakes crop up again, e.g., it is not clear why, during potentiometric titration of iron with dichromate, it is essential to add phosphoric acid. The method described for the titration of iodides with silver ions leads to large errors because of the adsorption of iodine ions by the precipitate. The addition of barium nitrate is recommended in order to increase the accuracy and stability of the electrode potentials. The author's suggestion of platinizing platinum electrodes in the determination of the pH of a solution with the quinhydrone electrode is a dubious one. Incidentally platinization is not described correctly. After platinization, the electrode in sulfuric acid should be the cathode and not the anode as the author advises.

The best chapter is chapter 10 which is devoted to polarography. The author also considers amperometric titration, since it is based on the same principles. This chapter, with regard to its lay out and from both theoretical and practical aspects, is the most successful, and does not call for any comment save that it is a pity the rest of the book is not on such a high level.

In chapter XI the thermoelectric and luminescence methods are discussed, together with analyses based on determination of the surface tension of solutions. The exposition of the first and third methods is strictly schematic. The luminescence method is described in more detail. Students should be able to gain sufficient elementary information for practical application of the method

On the whole it may be said that Yu. S. Lyalikov's textbook is a very useful and valuable book which fills a serious gap in Russian textbooks. In making a first attempt at describing the most important physico-chemical methods of analysis in a textbook, the author naturally could not avoid making a number of mistakes in the theory and in its practical applications, but these can be easily corrected in future editions.

P. K. Agasyan.

THE USE OF THE ULTRAVIOLET IN ANALYTICAL CHEMISTRY

2. QUALITATIVE MICROCHEMICAL ANALYSIS IN THE ULTRAVIOLET

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In microcrystalloscopic analysis, the form or color of the crystals formed by a particular ion on precipitation from a solution by a specific reagent is used as a means of detecting the ion. In some cases the formation of a precipitate can be taken as proof of the presence of the ion. Very few substances possess an observable color, particularly if the crystals are small. It should be noted that linking a colored ion with a definite cation or a colored cation with a definite anion does not solve the problem, since the given colored anion or cation can give colored compounds with other ions. Therefore conclusions as to the presence or absence of some particular ion can only be made on the basis of the crystal form of the precipitate formed. Crystal form however is by no means a certain criterion; the same compound can exist in different crystal forms depending on minor variations in the precipitating conditions, apart from the possibility of co-precipitation with other compounds; many compounds in general give precipitates with such small crystals that even with strong magnification they appear amorphous and their detection by microcrystalloscopic analysis is rendered difficult.

In cases where the substance to be analyzed is of a complex composition and includes several colored compounds, or when both the ions which compose the compound are colored the observed color is not equal to the sum of the colors of the components. In such cases it is necessary either to remove the interfering colored ion or to convert it into a colorless form (e.g. by conversion into a complex compound).

The new ultraviolet microscopy and particularly observation in ultraviolet light using the method of "color transformation" developed by Broomberg [1] has greatly extended the possibilities and scope of solving the above problems.

This method consists briefly in the substitution of the ultraviolet rays in the invisible image given by the objective of the ultraviolet microscope, by visible rays of different colors. In this way colored images of colorless objects are formed, the conditional colors of which are determined not by the normal visual spectrum but by the ultraviolet absorption spectra of the compound under examination.

As a result of the tinging of the ultraviolet absorption by the test compound a characteristic "ultraviolet" color is developed. For its detection a composite beam of light composed of red and ultraviolet rays is used. On projecting such a beam of light on to a fluorescent screen, the fluorescence of which is excited by ultraviolet of a definite wave length,

all the details of the test compound, which is located in the path of the beam and which absorbs ultraviolet rays, will assume different degrees of coloring according to the extent of absorption of the ultraviolet rays by the test compound.

In consequence of this the observer sees a shaded spot surrounded by the light of the fluorescent screen at those places where the rays not absorbed by the test compound have fallen. The shaded spot itself on the screen is colored red by the remaining rays.

The fluorescent screen is chosen so that it emits a white fluorescence under the action of ultraviolet light. This enables one to see the shadow of the test compound more clearly.

The color transformation method has two basic variants.

1) A photographic one, in which three photographs are taken in the ultraviolet for a chosen wave length and colored three different colors – red, green, and blue; the superimposed images of these photographs are simultaneously examined by means of a special apparatus – the chromoscope.

2) A visual one which is based on obtaining colored images on multi-colored fluorescent screens by means of ultraviolet light as described above.

It is possible therefore by means of the ultraviolet microscope to see colored crystals, which absorb ultraviolet light, even when they are completely transparent and colorless in visible light. Crystals which have different ultraviolet absorption spectra will accordingly have a different "ultraviolet" color in the field of vision of the microscope, by means of which they can be identified.

The use of the ultraviolet part of the spectrum for observation can essentially increase the number of microchemical reactions, since the strongest absorption spectral bands of many chemical compounds are located in this region of the spectrum. When observations are made in the ultraviolet it is often possible to use the absorption of a simple compound (and not the complicated compound absorption which it is usually necessary to obtain during microchemical analysis in the visible spectrum) and the analyst's problem reduces to a separation of ions from solution which have the same absorption (i.e. with the same ultraviolet color) as the test compound.

Thus for microchemical determination in the ultraviolet it is not the form of the crystals but their color which plays the chief role. The color can be used even in cases of "hidden" crystalline precipitates.

In the present article it is not our intention to replace microcrystalloscopic analysis in the visible part of the spectra by analysis in the ultraviolet. On the contrary in our view ultraviolet reactions may be regarded only as a useful supplement and for replacing those reactions in the visible spectrum which are inferior with regard to sensitivity and simplicity of detection in complex mixtures etc., i.e., our intention is to pursue the aim of constructing a relatively simple system of microchemical analysis, based on a combination of the usual reactions observed in visible light and in the ultraviolet, and certain luminescence reactions based on the observation of the luminescence of reaction products.

All three types of reaction are easily reproduced by means of the same universal apparatus – the ultraviolet microscope [2].

Apart from the two variants of the color transformation method described above it is possible to use a spectral method for the determination of the

nature of microcrystals by photographing their absorption spectra. By using a specially contructed spectral fitting for the ultraviolet microscope it is possible to get a microphotograph of the test compound together with the image of the spectrograph aperture and the spectrum lines on one photographic plate. Examples of such photographs are given in Fig. 1[1]. The mercury spectrum is included as a wave length scale. In this way it is possible to estimate the admission boundary of the crystals under test.

The spectrograms of crystals of $PbCl_2$ and $PbBr_2$ shown on Fig.1 show that crystals of these salts can be confidently distinguished from one another by their absorption spectra. If however substances are present in solution which have similar absorption spectra to those of the test material, it is necessary to perform a preliminary separation in order to avoid erroneous conclusions. The permitted amount of contaminant depends on the ratio of the ultraviolet absorption coefficients of the test sample and the contaminants.

Of the methods considered above, the most suitable one for carrying out large numbers of microchemical analyses is the visual method.

A PRK mercury lamp was used as the light source. An UFS-1 light filter which only transmits infra red and ultraviolet with wave length from 400-250 mμ was fitted on the microscope. The fluorescent screen had two layers, one of which was excited only by rays of wave length 365 mμ and has a blue colored fluorescence, while the other was excited by rays of wave length 313 mμ and fluoresced with a green color. As a result of mixing the direct red rays of the light source with green and blue from the screen, the microscope field was of a white color. Crystals which absorb the ultraviolet at $\lambda = 365$ mμ when placed in the field of vision were colored a purple-red color, while those absorbing $\lambda = 313$ mμ had a purple color and those absorbing at $\lambda = 254$ mμ were red. Thus the problem reduces to a selection of chemical reactions in which the reaction products absorb light of some definite wave length, i.e. to obtain for a particular reagent in a given mixture of substances, a characteristic ultraviolet "color" only for the chemical compound which it is necessary to determine. Consequently the absorption coefficients of the reaction products for the substances sought should be high in the wave length region of 365 and 313 mμ.

In spite of its simplicity and color sensitivity the visual method has one drawback, viz., it is impossible to distinguish by this method substances with close absorption limits. In such cases it is better to use the spectrographic method and the method of color photography, which permit a wide variation if necessary in the photographic conditions. These methods can be used when a more detailed study of the absorption spectra of microscopically small amounts of material is necessary.

Reactions for the detection of several cations either on their own or in the presence of each other which can be carried out using the visual method are considered below.

Identification of Alkali Metals. In order to identify the alkali metals we finally decided after a preliminary examination of many compounds to use ammonium hexachloroplatinate, ammonium cobaltinitrite, and potassium trithiosulphatobismuthate as possessing the highest absorption coefficients in the region $\lambda = 365$ mμ.

Reaction for Ammonium. For the detection of ammonium the characteristic absorption of the hexachloroplatinate and cobaltinitrite in the region $\lambda = 365$ mμ was used.

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[1]) See Plate, page 291.

In view of the fact that the corresponding compounds of sodium and potassium also exhibit strong absorption in this region of the ultraviolet, the determination of ammonia was carried out in a gas microcell.

a) As Hexachloroplatinate. A drop of test solution (NH_4Cl) was mixed in a gas cell with a drop of 20% NaOH. The top of the cell was closed with a quartz plate, on the inside face of which a drop of chloroplatinic acid was placed. The cell was gently heated on a microburner. Crystals of ammonium hexachloroplatinate appear instantly on the drop of chloroplatinic acid. These crystals on examination under the microscope are colored an intense red color because of the strong absorption in the ultraviolet.

This reaction is used in microcrystalloscopic analysis in the visible spectrum [3] with a fairly high sensitivity, but the presence of strong absorption in the ultraviolet enables the sensitivity to be increased considerably, as can be seen from a comparison of the results which we obtained for this reaction and those given in the literature for the same reaction in the visible spectrum.

Visible Spectrum		Ultraviolet Spectrum	
Limit of Identification	Limiting Concentration	Limit of Identification	Limiting Concentration
0.1 μg	1:10000	0.042 μg	1:24000

The presence of other cations in the solution containing ammonia does not hinder the detection of ammonia by the reaction when carried out as described above.

b) As the Cobaltinitrite. The determination of ammonia by reacting it with sodium cobaltinitrite $Na_3[Co(NO_2)_6]$ is carried out as with chloroplatinic acid. By this reaction 0.34 μg of ammonia can be detected at a limiting concentration of 1:3000. The presence of other ions in solution does not interfere.

Reactions for Potassium. On studying the character of the absorption by compounds of different cations with Karno's reagent $Na_3[Bi(S_2O_3)_3]$, we found that only potassium compounds absorb the ultraviolet at $\lambda = 365$ mμ. The other compounds absorb at 313 mμ and less. This enables potassium to be determined in the presence of other elements by means of Karno's reagent on a long wave screen, excited by light of $\lambda = 365$-380 mμ.

The Reaction was Carried Out as Follows. A drop of the test solution containing potassium was evaporated on a quartz microscope slide to dryness and a drop of the Karno reagent added to the residue. The appearance of needles colored red under the microscope, indicates the presence of potassium in the solution. This reaction which is also used for microcrystalloscopic analysis in visible light is made considerably more sensitive in the ultraviolet: the limit of identification becomes 0.7 μg instead of 2 μg and the limiting concentration can be decreased to 1:1500.

In spite of the fact that ammonium salts themselves do not give a precipitate with Karno's reagent and also do not absorb near the visible region, they appreciably decrease the sensitivity of this reaction.

Reactions for Sodium. The detection of sodium is carried out by a fluorescence method. As the result of the reaction between zinc uranyl acetate and sodium salts the yellow fluorescence becomes fixed in the precipitate of the octahedra of sodium zinc uranyl-acetate. The reagent solution itself does not fluoresce since chlorine ions and other ions have a quenching effect.

In order to carry out the reaction in the ultraviolet microscope fluorescent screens are used in conjunction with a UFS-2 light filter which transmits light of wave length $\lambda = 313$ mμ.

Procedure. A drop of test solution is placed on a quartz microscope slide side by side with a drop of zinc uranyl-acetate solution. After the two drops mix, the octahedra of sodium zinc uranyl-acetate separate out with a bright yellow-green color. This reaction is very sensitive. The limit of identification is 0.03 μg of Na and the limiting concentration 1:330000. Potassium and ammonium salts do not interfere.

Reactions for Iron. The reactions listed below are characteristic for ultraviolet microchemistry, since the detection of the element is carried out both in amorphous precipitates and in solutions by the formation of compounds which absorb the ultraviolet.

a) Detection of Iron in the Presence of Bivalent Tin. In the long wave length region of the ultraviolet only three hydrates exhibit selective absorption [i.e. of those studied by us (which included compounds of all the cations which are included in the general scheme of systematic qualitative analysis, with the exception of the rare elements)]. These are ferrous hydroxide, ferric hydroxide and stannous hydroxide. Ferrous hydroxide under these conditions is quickly oxidized by aerial oxygen. Thus there are two cations which mutually interfere during any attempt to detect one of them in the presence of the other in any given mixture. This may be overcome by using the property of stannous hydroxide of forming stannites with excess alkali; this is completely transparent to the ultraviolet while the ferric hydroxide absorbs ultraviolet intensely, so that it can be easily detected by the bright red color of the precipitate.

Procedure. A drop of the test solution is placed on a quartz microscope slide and 2-3 drops of 20% NaOH added. As a result only the ferric hydroxide remains as a precipitate, while the stannous hydroxide goes into solution as stannite. The precipitate is colored red under the microscope.

The limit of identification is 0.04 μg of iron at a limiting concentration of 1:25000, which exceeds the best microcrystalloscopic reaction in the visible spectrum, viz. the formation of Prussian blue in which the limit of identification is 0.07 μg of Fe at a limiting concentration of 1:14000 under the same conditions.

The limiting ratio of iron to tin at which this reaction is still possible for 0.04 μg iron is 1:125000.

b) Detection of Trivalent Iron in the Form of $FeAsO_4$. Of the arsenates, only ferric arsenate exhibits selective absorption in the long wave length part of the ultra violet. This enables ferric iron to be detected in the presence of other cations, and also in the presence of bivalent iron without a preliminary separation.

Procedure. A drop of the test solution is placed on a quartz microscope slide and a drop of potassium arsenate solution (0.5 N) placed side by side with it. When the two drops are mixed an amorphous precipitate is formed which contains all the cations with the exception of those of potassium, sodium and ammonium. If trivalent iron is present the precipitate is colored red under the microscope while if ferric iron is absent the precipitate is grey.

The limit of identification is 0.02 μg of iron at a limiting concentration of 1:70000. If the drop of test solution is preliminarily dried the sensitivity of this reaction increases considerably; it is possible to detect 0.005 μg of iron at a limiting concentration of 1:300000. This reaction is possible for the following ratios of other cations.

Fe^{3+} : Ba^{2+} = 1:75 for 0.04 μg Fe		Fe^{3+} : Co^{2+} = 1:30 for 0.04 μg Fe	
Fe^{3+} : Sr^{2+} = 1:45 for 0.04 μg Fe		Fe^{3+} : Cu^{2+} = 1:32.5" 0.04 μg Fe	
Fe^{3+} : Ca^{2+} = 1:40 for 0.04 μg Fe		Fe^{3+} : Hg^{2+} = 1:37.5" 0.04 μg Fe	
Fe^{3+} : Mn^{2+} = 1.27.5" 0.04 μg Fe		Fe^{3+} : Cd^{2+} = 1:12.5" 0.04 μg Fe	

c) Detection of Iron by Means of Ammonium Acetate. Acetates with the exception of ferric and ferrous acetates and silver acetate do not absorb in the ultraviolet. Absorption by acetates is displaced into the Schumann region. Silver acetate shows maximum absorption in the wave length range of 313-254 mμ. Moreover this compound decomposes rapidly under the influence of the ultraviolet to form metallic silver, which does not absorb in the ultraviolet. Thus it is possible to detect iron in the presence of all the remaining cations.

Procedure. A drop of saturated ammonium acetate is added to a drop of test solution. If iron is present the solution and precipitate of the basic acetate salts are colored red under the microscope. When no iron is present solution and precipitate are transparent to the ultraviolet. The reaction is fairly sensitive and enables 0.04 μg of iron to be detected at a limiting concentration of 1:24000. The limiting ratios of iron to other cations for which the reaction can be carried out without a preliminary separation are as follows.

$Fe:Mg^{2+}$ = 1:120 for 0.47 μg Fe		$Fe:Mn^{2+}$ = 1:118 for 0.47 μg Fe	
$Fe:Ba^{2+}$ = 1:750 " 0.47 μg Fe		$Fe:Cr^{3+}$ = 1:93 " 0.47 μg Fe	
$Fe:Ni^{2+}$ = 1:125 " 0.47 μg Fe		$Fe:Al^{3+}$ = 1:50 " 0.47 μg Fe	
$Fe:Co^{2+}$ = 1:126 " 0.47 μg Fe		$Fe:Zn^{2+}$ = 1:13 " 0.47 μg Fe	

d) Detection of Iron as $FeCl_3$. From the absorption curve of $FeCl_3$ (Fig.2) it is clear that this compound is very suitable for the direct identification of iron. No other chloride exhibits such sharp absorption in the neighborhood of the visible spectrum. This characteristic absorption was used by us for the identification of iron in test solutions.

Procedure. A drop of test solution is mixed with a drop of HCl. When iron is present the drop is colored a bright red under the microscope. Nor a single cation interferes with this reaction and its sensitivity is exceptionally high. It is possible to detect 0.006 μg of iron at a limiting concentration of 1:500000. Bismuth depresses the sensitivity as can be seen from the limiting ratios of iron to the other cations;

$Fe:Hg^{2+}$ = 1:581 for 4.7 μg Fe		$Fe:Ni^{2+}$ = 1:62 for 4.7 μg Fe	
$Fe:Bi^{3+}$ = 1:1 " 4.7 μg Fe		$Fe:Cr^{3+}$ = 1:37 " 4.7 μg Fe	
$Fe:Co^{2+}$ = 1:95 " 4.7 μg Fe			

Reactions for Cadmium in the Presence of Zinc. The majority of microcrystalloscopic reactions for cadmium in the visible part of the spectrum are unsuccessful when zinc is present, since zinc salts are formed as well as the characteristic cadmium precipitates, and they interfere with the color and form of the crystals of the cadmium salt, as a result of which the latter cease to be characteristic.

This drawback can be removed by using ultraviolet light.

a) Detection of Cadmium as Cadmium Sulfide. In contrast to zinc sulfide, cadmium sulfide strongly absorbs in the near ultraviolet. This enables cadmium to be detected without removal of zinc.

Procedure. A drop of sodium sulfide solution is added to a drop of the test

solution and the two mixed with a glass rod. If cadmium is present the large red crystals of cadmium sulfide can be seen under the microscope. 0.02 μg of cadmium can be detected at a limiting concentration of 1:44000 in the presence of zinc. The limiting ratio of cadmium to zinc is:

$$Cd^{2+}:Zn^{2+} = 1:20 \text{ for } 1.67 \ \mu g \ Cd^{2+}$$

b) Detection of Cadmium as Phosphate. Zinc phosphate does not absorb in the ultraviolet so that cadmium can be detected in the presence of zinc.

Fig. 2. Absorption curve for $FeCl_3$.

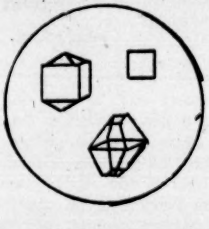

Fig. 3. Crystals of Cd-nitroprusside.

Procedure. A drop of Na_2HPO_4 solution is added to a drop of test solution and the precipitate formed examined under the microscope. If cadmium is present the precipitate is colored red.

By this method it is possible to detect 0.18 μg Cd^{2+} at a limiting concentration of 1:6000 and a ratio of $Cd^{2+}:Zn^{2+} = 1:40$ for 1.68 μg of cadmium.

c) Detection of Cadmium as the Nitroprusside. This reaction is the most sensitive of all the reactions for cadmium in the presence of zinc. It is based on the formation of characteristic crystals which absorb the ultraviolet at $\lambda = 365\text{-}313$ mμ (Fig.3).

Zinc in contrast to cadmium does not give a precipitate with sodium nitroprusside, and the solution does not absorb the ultraviolet at the given region of the spectrum.

Procedure. A drop of test solution is evaporated practically to dryness and a drop of a 1% solution of sodium nitroprusside added. The characteristic crystals which are formed are colored red when examined under the microscope.

The limit of identification is 0.01 μg of cadmium at a limiting concentration of 1:100000 and a limiting ratio of $Cd^{2+}:Zn^{2+} = 1:19$ for 5.6 μg of Cd^{2+}.

In conclusion I wish to express my thanks to Doctor E. M. Broomberg and Yu. V. Morachevsky for valuable advice and daily help in carrying out the work.

SUMMARY

1. A microchemical method of analysis, based on the application of the ultraviolet microscope is described together with several examples.

2. The advantages of ultraviolet microscopy over ordinary microscopy are demonstrated by means of a number of examples.

3. Qualitative microchemical reactions are described for ammonium, potassium, iron and cadmium.

4. A qualititative luminescence reaction for sodium is described.

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USE OF THE LIQUID INTERFEROMETER IN QUANTITATIVE ANALYSIS

III. THE STUDY OF DILUTE SOLUTIONS OF HYDROLYZABLE SALTS

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In previous articles [1,2] we have described the use of the interferometer method for the determination of the concentrations of dilute aqueous solutions of strong and weak electrolytes, using hydrochloric acid, caustic soda, oxalic, and acetic acids as examples. It was established in the course of this work that in the case of solutions of strong electrolytes within the concentration range employed, the so called phenomena of "breaks" can be observed and the curves relating the number of interference bands to the concentration for such solutions possess a stepwise character. Solutions of weak electrolytes do not exhibit the phenomena of "breaks", and the interference bands-concentration curves are straight lines, with some deviation from linearity for solutions of oxalic acid.

The aim of the present work is the study of the possibility of applying the interferometric method to the determination and control of the concentration of dilute aqueous solutions of hydrolyzable salts.

It could be assumed beforehand that interferometric measurements of these solutions would present certain difficulties which could only be solved experimentally. In addition, during investigations of sodium carbonate, and sodium bicarbonate solutions it was of interest to us to investigate the effect of hydrolysis on the linear relation between the number of interference bands and the concentration. The selection of these factors for investigation was determined by their significance in analytical practice and by the existing imperfect volumetric methods of determining the concentration of such solutions.

Study of Dilute Solutions of Sodium Carbonate. 25 solutions with concentrations ranging from 0.0025-0.16 N were prepared for interferometric measurements. Solutions of 0.001-0.1 N were prepared by dilution to standard volumes of an exactly 0.1 N solution of Na_2CO_3, and solutions greater than 0.1 N from a 0.2 N standard, prepared from chemically pure, dry Na_2CO_3 heated to a constant weight at 280-300°. The concentration of the Na_2CO_3 solutions were checked by potentiometric titration with HCl, the normality of which, 0.04812, was determined gravimetrically using $AgNO_3$ for precipitating the Cl ions.

Na_2CO_3 was titrated at 94-97° using a hydrogen electrode. The hydrogen was purified by passing it through washers of Ag_2SO_4, alkaline and acid $KMnO_4$ solutions.

It should be noted that although the potentiometric method of determining the equivalence point of Na_2CO_3 is more accurate and objective than the ordinary volumetric methods, nevertheless potentiometric titration is not free from errors. The liquid used for comparison was twice-distilled water from which the solutions used were prepared.

1) Deceased.

The Na_2CO_3 solutions were measured in a cell 19.91 mm long at 15±0.3°. The solutions were illuminated with white light, and the readings expressed on a drum scale in numbers of interference bands in a monochromatic green Hg light.

The other details of the method employed will not be dealt with further since they were described in detail in previous articles [3,4].

TABLE 1

Results of Measurements on Na_2CO_3 Solutions Expressed in Terms of N, Δn and $\Delta n/c$. Green Hg light, $\lambda = 546.07$ mμ at 15°

c (normality)	N' (Observed)	z	N (true)	$\Delta n \cdot 10^5$	$\frac{\Delta n}{c}$
0.002492	2.30	0	2.30	31.5	0.01266
0.010040	9.24	0	9.24	126.7	0.01262
0.015037	13.78	0	13.78	189.0	0.01257
0.020190	19.46	1	18.46	266.9	0.01254
0.039860	37.64	1	36.64	502.5	0.01261
0.044930	43.24	2	41.24	565.5	0.01258
0.080297	75.57	2	73.57	1009.0	0.01256
0.085490	81.19	3	78.19	1072.3	0.01254
0.10000	94.45	3	91.45	1254.1	0.01254
0.14634	135.81	3	132.81	1821.0	0.01245
0.16170	149.79	3	146.79	2013.0	0.01245
			Average		0.01256

Results are given in the abbreviated Table 1, from which a curve relating the number of interference bands to concentration can be derived (Fig.1).

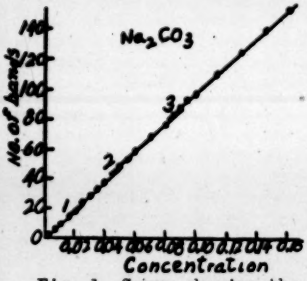

Fig. 1. Curve showing the relation between number of bands and concentration for Na_2CO_3 solutions.

In the table c is the concentration; N' – the observed number of bands; z – the number of bands corresponding to the number of breaks; N – the true number of bands with corrections for breaks; Δn – the difference between the refractive indices; and $\Delta n/c$ the ratio of Δn to the concentration.

Analysis of the results from the table and graph show that for the Na_2CO_3 concentrations employed there are only three breaks; the first between the 15.77 and 19.46 bands (for an additional solution which was measured with c = 0.01759 N corresponding to the 15.7 band, no break was established); the second between the 37.64 and 43.24 band and the third after 75 bands.

During preliminary measurements the presence of a fourth break at a concentration of 0.1146 N corresponding to the 101.48 band was postulated. However the presence of this fourth band could not be demonstrated by confirmatory experiments.

A comparison of the results for Na_2CO_3 solutions with similar measurements on NaOH solutions (see the abbreviated Table 2, taken from previous articles [1]) shows that while in the case of NaOH for a similar concentration range the presence

of eight breaks was established, with a new cycle starting after 15 bands, this periodicity was not observed from Na_2CO_3 solutions, for which the first break only appeared after the 15.77 band, the second after the 37.64 band and the third after 75 bands.

It may be postulated that this anomaly in the number of bands and the absence of any periodicity in the case of Na_2CO_3 solutions is a direct result of hydrolysis.

TABLE 2

Results for Measurements on NaOH Solutions Expressed in Terms of N, Δn, $\Delta n/c$. Green Hg light $\lambda = 546.07$ mμ at 20°.

c(molarity)	N' (observed)	z	N (true)	$\Delta n \cdot 10^6$	$\frac{\Delta n}{c}$
0.001010	0.85	0	0.85	11.6	0.01150
0.010330	8.65	0	8.65	118.6	0.01148
0.020376	18.08	1	17.08	234.3	0.01149
0.039941	35.48	2	33.48	459.2	0.01149
0.060306	53.43	3	50.43	691.5	0.01147
0.071213	63.60	4	59.60	817.3	0.01147
0.10033	88.67	5	83.67	1147.4	0.01143
0.11974	105.72	6	99.72	1367.5	0.01142
0.13970	123.22	7	116.22	1597.5	0.01143
0.16027	141.52	8	133.52	1831.0	0.01142

The value of Δn is known to be additive and is dependent both on the number as well as on the nature of the particles in solution. The accumulation in Na_2CO_3 solutions of HCO_3^- and OH^- ions together with Na^+ and CO_3^{2-}, increase the light refracting capacity of its solutions as compared with NaOH solutions. It is characteristic that for very dilute Na_2CO_3 solutions in which the extent of hydrolysis is most significant, the period for the first break is roughly the same as for NaOH solutions of the same concentration.

An increase in the concentration of the Na_2CO_3 solutions which is followed by a decrease in the degree of hydrolysis leads to a significant increase in the value of N and Δn as compared with the corresponding values for similar concentrations of NaOH. This is also confirmed by comparing the values of $\Delta n/c$ which on an average is equal to 0.01256 for Na_2CO_3 solutions and 0.01146 for NaOH solutions.

This anomalous behavior of dilute solutions of Na_2CO_3 in relation to hydrolytic effects was also established by Geffcken [5] who studied the concentration relationship between the apparent molecular volumes and apparent molecular refractions in dilute solutions.

In spite of this anomalous behavior of dilute solutions of Na_2CO_3 the experimentally determined curve relating the number of interference bands to concentration, as shown by confirmatory experiments, can be used successfully for the interferometric determination of unknown concentrations of Na_2CO_3 solutions.

The Study of Dilute Solutions of Sodium Bicarbonate. Interferometric measurements were made on 21 solutions of $NaHCO_3$ in the concentration interval 0.005-0.150 N. The solutions of the concentrations indicated were prepared by dissolving the corresponding amount of solid $NaHCO_3$ in twice distilled, carbon dioxide-free water. The solid salt was preliminarily checked for purity and content of $NaHCO_3$.

A final check on the concentration of the solutions prepared was carried out gravimetrically, taking into account necessary corrections for weighing in air and the specific gravity of water, the concentration being expressed in molarities (number of moles in 1 kilogram of solvent).

As in the previous instance measurements of $NaHCO_3$ were carried out in a cell 19.91 mm long at 20±0.1° with subsequent conversion of the results of measurements made in white light into numbers of interference bands in green Hg light.

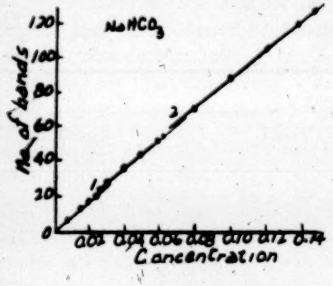

Fig. 2. Curve relating number of bands to concentration for $NaHCO_3$ solutions.

Results of these measurements are given in Table 3 in an abbreviated form, from which an interferometric curve relating the number of interference bands to concentration can be constructed.

Analysis of the tabulated results show that for $NaHCO_3$ solutions within the range of concentrations employed only two breaks could be established; the first at a concentration greater than 0.025 mol/1 between the 21.22 and 26.7 bands and the second at a concentration greater than 0.068 mol/1, i.e. between the 59.71 and 62.06 bands.

The anomaly in the number of breaks and the absence of periodicity in the breaks which was found for $NaHCO_3$ as well as for the Na_2CO_3 solutions examined previously, is probably the result of hydrolysis.

TABLE 3

Results of Measurements of $NaHCO_3$ Solutions Expressed in Terms of N, Δn and $\Delta n/c$ Green Hg light, $\lambda = 546.07$ mμ at 15° C.

c (molarity)	N' (observed)	z	N (true)	$\Delta n \cdot 10^6$	$\frac{\Delta n}{c}$
0.004596	3.98	0	3.98	54.6	0.01187
0.010182	8.80	0	8.80	120.6	0.01185
0.024655	21.22	0	21.22	291.0	0.01180
0.029862	26.70	1	25.70	352.4	0.01180
0.068565	59.71	1	58.71	805.1	0.01174
0.070132	62.05	2	60.05	825.5	0.01174
0.12079	105.37	2	103.37	1417.5	0.01174
0.14758	128.85	2	126.25	1731.2	0.01173
			Average		0.01178

In spite of this anomaly, the difference in light refraction expressed as interference bands N and Δn with increasing concentration increase for $NaHCO_3$ solution in approximately the same sequence as for similar concentrations of NaOH solutions.

A comparison of the values of N and Δn for approximately equal concentrations of $NaHCO_3$ and Na_2CO_3 shows a significant increase in their values for Na_2CO_3 solutions. It is characteristic that the average value of $\Delta n/c$ for Na_2CO_3 solutions is considerably higher than that for $NaHCO_3$ solutions.

In our opinion the results adduced above agree, and confirm the difference

in the hydrolytic effect for equal concentrations of Na_2CO_3 and $NaHCO_3$. Just as the hydrolytic effect should not interfere with the possibility of using the interferometric method for the determination of Na_2CO_3 concentrations, it should not interfere with the interferometric determinations of $NaHCO_3$ concentrations.

SUMMARY

1. Interferometric measurements have been made on dilute aqueous Na_2CO_3 and $NaHCO_3$ solutions.

2. From the results the values of Δn and $\Delta n/c$ for the same solutions for Hg light of $\lambda = 546.07$ mμ have been calculated.

3. Significant deviations in the appearances of breaks in the interferometric curves of $\underline{N}$ against $\underline{c}$ was observed for Na_2CO_3 and $NaHCO_3$ solutions as compared with NaOH solutions.

4. It has been shown that the difference in these curves and the greater increase in the values of N, Δn and $\Delta n/c$ for Na_2CO_3 solutions and the smaller increase in the corresponding values for $NaHCO_3$, as compared with similar concentrations of NaOH are determined by the different extents of hydrolysis of these electrolytes.

5. Using Na_2CO_3 and $NaHCO_3$ as examples it has been confirmed experimentally that the interferometric method can be used for the determination and control of the concentrations of hydrolyzable salts.

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THERMODYNAMIC CRITERIA OF THE APPLICABILITY OF CHEMICAL REACTIONS OF VOLUMETRIC ANALYSIS

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There is no clear formulation in contemporary literature of the requirements which must be satisfied by chemical reactions used in volumetric analysis from the thermodynamic point of view. Most authors confine themselves to general observations about "reactions which proceed quantitatively", without investing this concept with any concrete content. Meanwhile, it is possible as shown below, to formulate clearly criteria for the applicability of different reactions in volumetric analysis by adopting a thermodynamic approach. Moreover, thermodynamic consideration of reactions which are the bases of volumetric-analytical determinations, enables all the branches of volumetric analysis to be combined and considered from a single view point.

As a rule in volumetric analysis reversible reactions are used in which the equilibrium is strongly displaced towards the side where formation of the reaction products occur:

$$n_1A_1 + n_2A_2 \rightleftarrows n_1'B_1 + n_2'B_2. \qquad (I)$$

From our point of view it is essential to follow the changes in concentration of two substances (the titrant and the material to be titrated) denoted by A_1 and A_2. A third component can participate in this reaction (H and OH ions), nevertheless in actual conditions the concentration of the third component is low and does not change very much during titration. In the majority of cases the change in ionic strength during titration is insignificant and therefore concentrations can be used instead of activities.

Of particular interest to the analytical chemist is the ratio at the equivalence point; at this point the respective reaction products (B_1 and B_2) which are formed in stoichiometric ratios are subject to a partial conversion into the original reactants:

$$n_1'B_1 + n_2'B_2 \rightleftarrows n_1A_1 + n_2A_2. \qquad (Ia)$$

The equilibrium constant of this reaction is a very important thermodynamic quantity which is related to the standard change in the thermodynamic potential (ΔZ°) by the relation:

$$\Delta Z^\circ = - RT \ln K. \qquad (1)$$

At 25° this equation becomes:

$$\Delta Z^\circ = - 1364 \log K \qquad (1a)$$

Let us consider the change in thermodynamic potential for reaction (Ia) in a system where the ratio of all the reactants is equal to the ratio of the stoichiometric coefficients of equation (Ia), i.e.

$$C_{A_1} = n_1a \quad C_{A_2} = n_2a \quad C_{B_1} = n_1'a \quad C_{B_2} = n_2'a. \qquad (2)$$

If we substitute these values of the concentrations in the equation for the

chemical reaction isotherm, we get[1]:

$$\Delta Z = RT\left(\ln\frac{(n_1a)^{n_1}(n_2a)^{n_2}}{(n_1'a)^{n_1'}(n_2'a)^{n_2'}} - \ln K\right). \qquad (3)$$

Equation (3) can be transformed by substituting logarithms to the base ten instead of the natural logarithms, multiplying out the logarithm and substituting numerical values for R and T (298° K):

$$\Delta Z = 1364[n_1 \log n_1 + n_2 \log n_2 - n_1' \log n_1' - n_2' \log n_2' + (n_1 + n_2 - n_1' - n_2') \log a - \log K]. \qquad (4)$$

The following abbreviations are then used:

$$\sum n \log n = n_1 \log n_1 + n_2 \log n_2 - n_1' \log n_1' - n_2' \log n_2', \qquad (5)$$

$$\sum n = n_1 + n_2 - n_1' - n_2', \qquad (6)$$

$$pK = -\log K. \qquad (7)$$

So that equation (4) may be rewritten in the condensed form:

$$\Delta Z = 1364\left(\sum n \log n + \log a \sum n + pK\right) \qquad (8)$$

or

$$\Delta Z = 1364\left(\sum n \log n + \log a \sum n\right) + \Delta Z^{\circ}. \qquad (9)$$

At the equivalence point the ratio of the concentration of reaction products B_1 and B_2 is equal to the ratio of the corresponding stoichiometric coefficients (n_1' and n_2').

The concentrations of these substances differ only by very little from the values calculated on the assumption of the absence of any conversion into the original reactants. The original reactants, as a result of reaction (1a) are also formed in strictly stoichiometric ratios. We shall introduce the following designations for the concentrations of the substances at the equivalence point[2]:

$$\bar{C}_{A_1} = n_1x \quad \bar{C}_{A_2} = n_2x \quad \bar{C}_{B_1} = n_1'a \quad \bar{C}_{B_2} = n_2'a. \qquad (10)$$

After substituting these values in the equation for the equilibrium concentrations of reaction (Ia) we get:

$$\frac{(n_1x)^{n_1}(n_2x)^{n_2}}{(n_1'a)^{n_1'}(n_2'a)^{n_2'}} = K. \qquad (11)$$

On taking logarithms of this equation and using the abbreviations (5) and (6) we get:

$$\sum n \log n + (n_1 + n_2) \log x - (n_1' + n_2') \log a = -pK. \qquad (12)$$

This equation can be used primarily for calculating the concentrations of reactants (A_1 and A_2) at the equivalence point. In accordance with the accepted designations:

$$\log\bar{C}_{A_1} = \log n_1 + \log x; \qquad (13)$$

$$\log\bar{C}_{A_2} = \log n_2 + \log x. \qquad (13a)$$

If we substitute the value of $\log x$ from equation (12) in these equations and simplify, we get an universal equation for calculating the concentrations of the

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1) From here onwards we are dealing with reactions which occur in condensed systems.
2) The equilibrium concentrations of B_1 and B_2 differ only very slightly from the initial concentrations because of the quantitative course of reaction (I).

reactants at the equivalence point:

$$\log \bar{C}_{A_1} = \frac{(n_1' + n_2')\log a - pK - \sum n \log n + (n_1 + n_2)\log n_1}{n_1 + n_2} \qquad (14)$$

or

$$\log \bar{C}_{A_1} = \frac{n_1' \log C^0_{B_1} + n_2' \log C^0_{B_2} + n_2 \log \frac{n_1}{n_2} - pK}{n_1 + n_2} \qquad (14a)$$

These equations can be used for calculating the concentrations of the reactants at the equivalence point for any volumetric method of analysis. The possibility of using any given reaction in volumetric analysis is determined by the magnitude of the reconversion of the reaction products (B_1 and B_2) into the reactants (A_1 and A_2). The extent to which this reconversion occurs is given by the relation:

$$\alpha = \frac{x}{a} . \qquad (15)$$

The value of this ratio defines the theoretical limit of the practicable accuracy for a given reaction. E.g., an accuracy of determination of $\pm 0.1\%$ can be achieved under conditions such that the extent of reconversion of the reaction products into the reactants (α) does not exceed 0.001. If decomposition of the reaction products to give reactants exceeds this value, then the accuracy of $\pm$ 0.1% cannot be achieved at the given temperature. Log α can be calculated from Equation (12). It is equal to:

$$\log \frac{x}{a} = \frac{-pK - \log a \sum n - \sum n \log n}{n_1 + n_2} \qquad (16)$$

By means of this equation the limiting practicable accuracy for any volumetric method of analysis can be calculated.

Since the accuracy of volumetric determinations amounts to $\pm 0.1\%$, then the conditions for realizing this accuracy can be formulated as follows:

$$\log \frac{x}{a} \leqslant -3 \qquad (17)$$

The value of log x/a can be taken from Equation (16), from which:

$$pK + \log a \sum n + \sum n \log n \geqslant 3(n_1 + n_2). \qquad (18)$$

By comparing this equation with Equation (8), we get:

$$\Delta Z \geqslant 3 \cdot 1364 \cdot (n_1 + n_2). \qquad (19)$$

The inequalities of (17), (18), and (19) express the possibility of carrying out a titration based on the use of a given reaction with an accuracy of $\pm$ 0.1%. A more simple formulation of this possibility can be derived from Equation (19).

The change in thermodynamic potential in process (1a), in a system where all the reactants are at concentrations corresponding to those at the equivalence point, should exceed a definite value. E.g., in a simple case during the formation of a substance AB, the value of ΔZ should exceed 8184 calories.

The possibility of using a given reaction in volumetric analysis is determined by the values of the equilibrium constant of reaction (Ia) (it should have a minimum value), and by the concentration of the reactant at the equivalence point (maximum values).

All the equations given above and all the arguments advanced are true for titration reactions and do not apply to reactions preceding titration (preliminary precipitations, separation, changes in the degree of oxidation, etc.).

Let us consider one of the most important and most often used special cases – a reaction of the type[1]:

$$A + nB = ABn, \qquad (II)$$

in this case $\sum n \log n = n \log n$ and $\sum n = n$.

Equations (14) and (18) are simplified considerably in this special case. If we substitute and take into account (2), we get

$$\log \bar{C}_A = \frac{\log C_A^0 - pK - n \log n}{n + 1}; \qquad (14a)$$

$$\log \bar{C}_B = \frac{\log C_B^0 - pK}{n + 1}; \qquad (14b)$$

$$pK + n \log C_B^0 \geqslant 3(n + 1) \qquad (18a)$$

In these equations $\bar{C}_A$ and $\bar{C}_B$ represent the equilibrium concentrations, and C_A^0 and C_B^0 the hypothetical concentrations of A and B at the equivalence point under such conditions that there is no interaction between them. C_A^0 and C_B^0 are the initial concentrations of A and B.

We shall demonstrate the applicability of these equations for determining the possibility of using different reactions in volumetric analysis and for calculating the ratios at the equivalence point for a number of cases. For the titration of a strong acid with a strong base or vice versa the reaction proceeds according to the equation:

$$H^+ + OH^- = H_2O. \qquad (III)$$

The concentration of water formed during this reaction remains practically unchanged during titration, and the concentration of water is therefore not included in the equation for the equilibrium constants, in this case:

$$n_1 = n_2 = 1, \quad \sum n = 2, \quad \sum n \log n = 0.$$

Here, $pK = 14$.

Substituting these values in Equations (14) and (18) we get:

$$\log \bar{C}_H = -7, \qquad \log C_H^0 \geqslant -4. \qquad (18b)$$

In reaction (III), therefore, the concentrations of the reactants should be more than 0.0001 M.

The titration of weak acids with strong bases proceeds in the majority of cases according to the equation:

$$HA^z + OH^- = A^{z-1} + H_2O, \qquad (IV)$$

The equilibrium constant for reactions involving the conversion of A^{z-1} into the reactants is equal in this case, as is well known, to the hydrolysis constant:

$$K_h = \frac{K_W}{K_A}, \qquad (20)$$

where K_W is the ionic product of water, and K_A is the ionization constant of acid HA^z. From which it follows for process (IV):

$$pK_h = 14 - pK_A. \qquad (21)$$

The concentration of H_2O is not included in the equation of the law of mass

[1] From this point onwards we shall consider the equilibrium constants of the reverse reaction, i.e., the decomposition of AB_n into its components in this actual given instance.

action for Reaction (IV), and according to Equation (14a) for the equivalence point we get the well-known relation:

$$\log \bar{C}_{OH} = \frac{\log C^0_{OH} + pK_A - 14}{2} . \qquad (14c)$$

From Equation (18a) the following conditions for the accurate titration of weak acids can be derived:

$$pK_A - \log C^0_{OH} \leqslant 8. \qquad (18c)$$

If decinormal solutions are used and the volume is assumed to remain unchanged during the titration,

$$pK_A \leqslant 7.$$

It is therefore only possible to titrate with accuracy those acids whose ionization constants are greater than 10^{-7} ($pK_A \leqslant 7$), e.g., the following acids: HF (3.14); H_2S (6.48); H_2CO_3 (6.43); H_3PO_4 (2.12); $H_2PO_4^-$ (7.21); HCOOH (3.75); CH_3COOH (4.76), etc. (The values of pK_A are given in brackets).

Exact titrations of the following acids cannot be realized in 0.1 N solutions: HCN (9.14); H_3BO_3 (9.24); C_6H_5OH (9.89); HCO_3^- (10.24); H_2O_2 (11.62); HIO_3 (10.7); HPO_4^{2-} (12.3); HS^- (14.70), etc. From Equation (16) it follows, e.g., that H_3BO_3 in 0.1 M solution can be titrated with an accuracy of $\pm$ 1.3%. For the titration of salts of weak acids with strong acids according to the equation

$$A^{z-1} + H^+ = HA^{z-1} \qquad (V)$$

the equilibrium constant is equal to the ionization constant of the acid HA^z. By using Equation (14a) for the hydrogen ion concentration at the equivalence point, we get the following relation:

$$\log \bar{C}_H = \frac{\log C^0_H - pK_A}{2} . \qquad (14d)$$

The possibility of titrating according to Equation (V) is determined by Equation (18a); in this case we get

$$pK_A + \log C^0_H \geqslant 6 . \qquad (18d)$$

If 0.1 N solutions of acid are used, then

$$pK_A \geqslant 7.$$

When using decinormal solutions it is possible to attain the necessary accuracy ($\pm$ 0.1%) only for salts of acids for which the ionization constant is less than 10^{-7}.

Examples are given below of anions, the concentration of which can be determined in 0.1 N solution (the values for pK_A are given in brackets): CN^- (9.14); CO_3^{2-} (10.24); HCO_3^- (6.43); HS^- (6.48)[1]; C_6H_5OH (9.89), etc. It is impossible to realize by means of Equation (V) an exact determination in 0.1 N solutions of the ions: F^-, CH_3COO^-, $C_6H_5COO^-$, etc. From Equation (16) it follows, e.g., that an acetate in 0.1 M solution can be titrated with an accuracy of $\pm$ 1.3%. For weak bases reacting with strong acids according to the scheme:

$$B + H^+ = BH^+, \qquad (VI)$$

the equilibrium constant of the reaction is determined by the conversion of BH^+ into the original components, and is equal to:

$$K = \frac{K_W}{K_B} \qquad (20a)$$

1) For HCO_3^- and HS^- the accuracy of the titration is approximately 0.2%.

from which

$$pK = 14 - pK_B \quad . \tag{21a}$$

The hydrogen ion concentration at the equivalence point can be calculated by means of Equation (14a):

$$\log \bar{C}_H = \frac{\log C_H^0 + pK_B - 14}{2} \quad . \tag{14e}$$

Substituting the value of pK in Equation (18c), then in this case we get:

$$pK_B - \log C_H^0 \leqslant 8. \tag{18e}$$

For decinormal solutions: $pK \leqslant 7$. According to (IV) it should be possible to titrate accurately by means of 0.1 N solutions only in those cases when the ionization constant of the base is fairly high and exceeds 10^{-7}. This requirement is satisfied by NH_3 (4.75), $C_2H_5NH_2$ (3.25), $HOCH_2CH_2NH_2$ (4.56), etc. It is not possible to titrate the following bases accurately in 0.1 N solution by means of a strong acid: pyridine (8.85); aniline (9.42); acetamide (12.60); urea (13.82); thiourea (14.96); etc. (the figures in brackets are the pK_B values).

Complex-formation reactions, which are being used more widely of late in volumetric analysis, proceed according to the scheme:

$$M^{z+} + nA^{x-} = [MA_n]^{z-nx} \quad . \tag{VII}$$

The equilibrium constant of the decomposition reaction of the complex ion to form its components is the instability constant (K_n), and accordingly $pK = pK_H$. The concentrations of the metal ion (M^{z+}) and the addendum A^x at the equivalence point can be calculated from Equation (14a). In this case we have:

$$\log \bar{C}_{M^{z+}} = \frac{\log C_M^0 - pK_H - n \log n}{n + 1} \quad ; \tag{14f}$$

$$\log \bar{C}_{Ax-} = \frac{\log C_A^0 - pK_H}{n + 1} \quad . \tag{14g}$$

The possibility of using complex-formation reactions for volumetric analysis calculation is determined by the following inequality which is derived by substitution of the value of pK_H in the inequality (18a)

$$pK_H \geqslant 3n + 3 - n \log C_B^0 \quad . \tag{18f}$$

If the concentration of the original solution of the addendum (A^{x-}) is 0.1 M, then

$$pK_H \geqslant 4n + 3,$$

i.e., for complexes with different coordination numbers pK_H should be greater than some definite value. In the case of a salt of the type MA^{z-x}, $pK_H \geqslant 7$; for a coordination number of 2, $pK_H \geqslant 11$; for a complex of the type MA_3^{z-3x}, $pK_H \geqslant 15$, and, finally, in the case of a complex of the type MA_4^{z-4x}, $pK_H \geqslant 19$.

Titrations based on the formation of the following complexes can be carried out in solutions 0.1 M with respect to the addendum (the values of pK_H are given in brackets): $FeHPO_4^+$ (9.35); $HgCl_2$ (12.8); $HgBr_2$ (17.3); $Ag(CN)_2^-$ (21); $Cu(NH_2CH_2COO)_2$ (15.3); $Zn(OH)_3^-$ (14.4); $Cd(CN)_4^{2-}$ (18.8); $TlCl_4^-$ (18.4);, etc.

Accurate titrations on the basis of the formation of the following complexes, however, cannot be carried out in 0.1 M solution with respect to the addendum: CdI_4^{2-} (6.0); $Cd(S_2O_3)_3^{4-}$ (7.0); $FeCNS^{2+}$ (2.40); $Cu(NH_3)_4^{2+}$ (12.7), etc.

The relations given above are also applicable for calculation when precipitation reactions are used in volumetric analysis. Almost all precipitation

reactions which are in use proceed as follows:

$$M^{z+} + nA^{x-} = MA_n\downarrow \quad . \qquad \text{(VIII)}$$

The concentrations of the metal cations and anions A^{x-} at the equivalence point can be calculated by substituting the respective values in Equation (14).

The decomposition of the precipitate formed to give the original reactants is characterized by the solubility product of the salt, MA_n(Lp). The reciprocal of the logarithm of the solubility product is denoted by pLp. After substitution of this value in Equation (14) and simplifying, we get:

$$\log \bar{C}_M = \frac{-pLp - n \log n}{n + 1} \quad ; \qquad \text{(14h)}$$

$$\log \bar{C}_A = \frac{-pLp + \log n}{n + 1} \quad . \qquad \text{(14i)}$$

The possibility of using a given precipitation reaction for volumetric analysis is determined by the Inequality (18). For reaction (VIII):

$\sum n \log n = n \log n$, a $\sum n = n + 1$. Having worked out (2), substituting in Equation (18) all the values, and simplifying, we get:

$$pLp + n \log C_A^o + \log C_M^o \geqslant 3(n + 1). \qquad \text{(18g)}$$

If solutions are used with $C_M^o = 0.1$ and $C_x^o = 0.1\ n$, we get

$$pLp + n \log n \geqslant 4(n + 1).$$

For salts of type MA, pLp should be greater than 8, and in the case of salts of type MA_n, pLp should be greater than 11.4. It should be borne in mind that we are considering titrations to an accuracy of 0.1% of solutions 0.1 N or 0.1 M with respect to the metal. The formation of the following salts satisfies this requirement: AlCl (9.81); AgBr (12.11); AgI (15.82); $BaSO_4$ (9.97); $PbCrO_4$ (13.74); Hg_2Cl_2 (17.96); Hg_2Br_2 (22.3); $Hg_2(CNS)_2$ (19.52); $Pb(IO_3)_2$ (12.52), etc. The formation of the following salts does not satisfy this requirement: $SrSO_4$ (6.55); TlCl (3.72); $PbBr_2$ (5.20); PbI_2 (8.06), etc.

Equations (16), (18), and (19) can also be used for calculations involving oxidation-reduction reactions. Let us consider one of the most commonly used cases:

$$n_1 \text{ oxid.}_1 + n_2 \text{ reduc.}_2 = n_1 \text{ reduc.}_1 + n_2 \text{ oxid.}_2. \qquad \text{(IX)}$$

In this case $\sum n \log n$ and $\sum n$ become zero. The logarithm of the equilibrium constant is related to the oxidation-reduction potential by the simple relation:

$$pK = \frac{(\pi_2 - \pi_1)v}{0.058} \quad . \qquad \text{(22)}$$

Equation (22) can be applied to reactions which proceed at a standard temperature; π_2 and π_1 are the oxidation-reduction potentials, and v is the number of donated (or accepted) electrons.

Using Equation (16), we find that at the equivalence point

$$\log C^o_{\text{oxid.}_1} = \frac{(\pi_2 - \pi_1)v}{0.058(n_1 + n_2)} + \log C^o_{\text{oxid.}} \qquad \text{(14j)}$$

In order to establish the possibility of using any given oxidation-reduction reaction in volumetric analysis, we use Equation (18). In this particular case it is transformed into the following equations:

$$\frac{(\pi_2 - \pi_1)v}{0.058} \geqslant 3(n_1 + n_2) \qquad \text{(18h)}$$

and

$$\pi_2 - \pi_1 \geqslant \frac{0.174(n_1 + n_2)}{v} \quad . \qquad (181)$$

The possibility of using a given reaction in volumetric analysis is determined by the potential difference. A change in pH and other conditions is connected with a change in the oxidation-reduction potentials, and is taken into account in the value of the normal potentials, which are related to a strictly defined pH value.

In conclusion the author should like to observe that is is possible to consider all volumetric analysis methods from one point of view by means of the equations adduced. We think that the wide use of the Inequalities (18) and (19) will considerably facilitate the search for new analytical reactions and will enable the possible limits of the application of reactions already in use in volumetric analysis to be defined more clearly.

SUMMARY

1. A universal equation for calculating the concentrations of the reactants at the equivalence point is proposed. This equation is applicable for calculating concentrations in reactions involving neutralization, complex formation, precipitation, and oxidation-reduction, respectively.

2. Universal inequalities are proposed which determine the possibility of using any given reaction in volumetric analysis, in which a determination can be carried out with a given degree of accuracy (examples are given of reactions in which accuracies of $\pm$ 0.1% are required). These inequalities are applied to concrete cases in methods based on neutralization, complex formation, precipitation, and oxidation-reduction reactions, respectively.

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A COLORIMETRIC METHOD FOR THE DETERMINATION OF IRON

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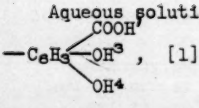
Aqueous solutions of protocatechuic acid (3,4-dihydroxybenzoic acid-1) —  , [1], and of protocatechuic aldehyde [2] are known to give a very characteristic reaction with ferric chloride: a green color appears initially, which on addition of a weak alkali solution first turns into a violet color and finally into a red color.

Lutz [3] used protocatechuic acid for detecting iron. The author shows that by means of an aqueous solution of protocatechuic acid it is possible to detect 0.24 μg of Fe^{3+} in 1 ml of solution in a weakly acid medium at a limiting dilution of 1:4,200,000, while in a weakly alkaline medium 0.1 μg Fe^{3+} in 1 ml can be detected at a limiting dilution of 1:10,000,000. Protocatechuic acid reacts in a similar manner with salts of Tl and Ce.

In the present work the reactive capacity of protocatechuic aldehyde with salts of trivalent iron has been examined, and the sensitivity and specificity of the given reaction determined. It was established that the color obtained at low concentrations 25 - 0.5 μg of trivalent iron in 1 ml of solution with protocatechuic aldehyde in alkaline media follows the Lambert-Beer law. This fact was used as the basis of a new colorimetric method for the determination of iron in metallic aluminum and zinc and in salts of the alkali and alkaline-earth metals respectively.

EXPERIMENTAL

Detection of trivalent iron in weakly acid media. To 1 ml of the test solution are added 0.1 ml of 1% HCl, 0.1 ml of a 0.25 aqueous solution of protocatechuic aldehyde, and the mixture shaken. After 5-10 minutes a color is observed. If trivalent iron is present, the color developed is an intense green color for large concentrations, and a pale violet color for low concentrations.

0.5 μg of Fe^{3+} in 1 ml solution can be detected in this way in a weak acid medium at a limiting concentration of 1:2,000,000.

Detection of trivalent iron in weakly alkaline media. To 1 ml of the test solution are added 0.1 ml of 1% ammonia, 0.1 ml of a 0.25% aqueous solution of protocatechuic aldehyde, and the mixture shaken. A blank test is made simultaneously, i.e., the same volumes of the above reagents are added to 1 ml of distilled water, the mixture shaken and after 5-10 minutes the color of the test solution and blank solution are compared. If Fe^{3+} is present in large amounts the color developed is an intense red, while at low concentrations the color is orange yellow. The blank is simply colored yellow. When the reaction is carried out in weak alkaline media it is impreative that a blank be done because the reagent itself gives a yellow color with alkali.

In weak alkaline medium 0.2 μg of Fe^{3+} in 1 ml solution can be detected at a limiting concentration of 1:5,000,000.

The following cations and anions do not react with protocatechuic aldehyde and therefore do not interfere with the detection of trivalent iron-alkali and alkaline earth metals: Mg, Be, Al, Zn, Cd, Cu^{2+}, Hg^{2+}, Mn^{2+}, Co, Ni, Th^{4+}, Zr^{4+}, La^{3+}, I^{+}, Er^{3+}, Nb, Ta, Au, Pd, Pt, Ti^{2+}, Sn^{2+}, Ag, AsO_4^{3+}, PO_4^{3+}, WO_4^{2-}, Fe^{2+}.

Bivalent iron does not react with either protocatechuic acid or aldehyde. Lutz [3] is in error when he indicates that protocatechuic acid reacts with bivalent iron.

Elements which form precipitates with alkali do not interfere with the detection of iron, since if iron is present a red or orange yellow color develops in the transparent layer above the precipitate, while in the blank a yellow color appears. Naturally it is best to use approximately the same amounts of the elements which form precipitates with alkali in the blank. The elements enumerated above do not interfere with the detection of iron at ratios to Fe^{3+} of 3,000 : 1.

Only MoO_4^{2-}, VO_3^{-}, and Ce^{3+} react with protocatechuic aldehyde. Molybdenum reacts with aqueous solutions of protocatechuic aldehyde only in neutral media, giving an orange color at large concentrations and a pale yellow one at low concentrations. The sensitivity of this reaction is 0.2 μg of molybdenum in 1 ml at a limiting concentration of 1:5,000,000. Molybdenum does not react in weakly acid solution.

Vanadium salts react in neutral media to give a dark brown color, and at low concentrations a violet brown color.

In weak HCl solution vanadium initially gives a rose color which is transformed after 10-15 minutes into a yellow color.

The sensitivity of the reaction for vanadium both in neutral and in acid media is 1 μg of vanadium in 1 ml solution at a limiting concentration of 1:1,000,000.

Salts of trivalent cerium only react with protocatechuic aldehyde in a weak ammonia solution, giving a red-brown color at high concentration and a yellow-brown color at low concentrations.

The sensitivity of the reaction is 4 μg of Ce^{3+} in 1 ml solution at a limiting concentration of 1:250,000.

Ce^{3+} does not react in acid media.

Colorimetric determination of trivalent iron. Standard solutions of trivalent iron are prepared containing 0.02 g Fe in 1 ml. 0.25 μg of chemically pure metallic iron is dissolved in 5 ml nitric acid diluted with 10 ml of water. The solution thus obtained is diluted to 1 liter (Solution A), 40 ml Solution A are diluted to 500 with water (Solution B). Solution B contains 0.02 mg of Fe in 1 ml.

Colorimetric determination of iron in metallic aluminum.

0.1 - 0.2 g of metallic aluminum (according to the iron content) is weighed out into a 50 ml beaker and 10 ml HCl (1:3) added. The beaker is covered with a watch glass, and slightly heated by alternately placing it on a hot plate and removing it until all the aluminum is dissolved when the solution is cooled to 40-50° and 1 ml of 3% H_2O_2 added to oxidize the Fe^{2+}. The beaker and its contents are then placed on a hot plate and the contents boiled for 5-10 minutes to decompose excess H_2O_2. The contents are transferred quantitatively to a 100 ml standard flask, made up to the mark with water and carefully mixed. 5 or 20 ml aliquots (according to the amount of iron) are transferred to a 50 ml standard to which 2 ml of a 0.25% solution of protocatechuic aldehyde is added.

The solution in the flask becomes colored green immediately. A solution of 10% NaOH is then added dropwise with continuous shaking until all the aluminum hydroxide precipitate has dissolved. When this has been accomplished the color of the solution and precipitate changes from a green through violet to a raspberry or orange-yellow color.

When all the precipitate has dissolved, water is added to the colored, transparent solution to bring the volume up to the mark, after which it is carefully shaken. The solution is then ready for color comparison.

At the same time 5 or 10 ml of the standard iron solution - solution B - are introduced respectively into a 50 ml standard flask, 2 ml reagent, and 0.5 ml of 10% NaOH are added and the whole made up to volume with water and throughly mixed. The color of the test solution and blank are compared in a Duboscq colorimeter.

By means of this method the iron content of 12 samples of aluminum was determined (Table 1). For comparison the iron content was determined in the same samples by a colorimetric method based on sulfosalicylic acid in ammoniacal solution by means of which both Fe^{2+} and Fe^{3+} were determined colorimetrically [4, 5, 6, 7].

It is necessary to point out that it is best to determine iron colorimetrically by means of protocatechuic aldehyde in alkaline solution. In acid media the color intensity (green light) is small for low concentrations, so that colorimetric determination is difficult.

TABLE 1

Iron content in percent		
Results of factory laboratory analysis	Colorimetric determination	
	With protocatechuic aldehyde	With sulfosalicylic acid [1]
0.79	0.80	0.76
0.35	0.34	0.32
0.28	0.28	0.27
0.14	0.13	0.13
1.57	1.58	1.60
0.29	0.32	0.30
0.18	0.20	0.21
0.13	0.15	0.15
0.14	0.15	0.13
0.82	0.85	0.80
0.70	0.69	0.68
0.93	1.06	1.09

The results in Table 1 show that the colorimetric determination of iron with protocatechuic aldehyde in alkaline solution gives results in good agreement both with the results of the sulfosalicylic acid method and with the results of factory analyses. The method proposed can be succesfully applied to the determination of iron in metallic aluminum. One determination takes 40-50 minutes.

The colorimetric determination of iron in metallic zinc.

1 g of metallic zinc or powder is put into a 50 ml beaker, 15 ml of dilute HCl are added (1:2) and the beaker covered with a watch glass. The beaker is gently heated by alternately placing it on and removing it from a hot plate, until the zinc has dissolved completely, when it is cooled to 40-50° and 1 ml of H_2O_2 added to oxidize the Fe^{2+}. The beaker's contents are boiled for 5-10 minutes to remove excess H_2O_2 and the contents finally quantitatively transferred to a 50 ml standard flask. 2 ml of a 0.25% solution of protocatechuic aldehyde is added and 10% NaOH solution added dropwise until all the zinc hydroxide dissolves. The colored, transparent solution thus obtained is made up to the mark with distilled water and carefully shaken, after which it is ready for colorimetric comparison.

At the same time 5 ml of the standard iron solution - Solution B - is introduced into a standard flask together with 4 ml reagent and 0.5 ml of a 10% solution of NaOH, made up to the mark with water and carefully shaken. The colors of the test and blank solution are compared in a Duboscq colorimeter. 0.004% iron can be determined in 1 g of zinc by this method. Duplicate determinations give good agreement

1) Part of the work with sulfosalicylic acid was carried out by A.I.Zaikin, to whom I express my thanks

In order to check the accuracy of the method experiments were carried out in which metallic zinc samples previously analyzed were taken and known amounts of iron in solution added after dissolution of the zinc. After oxidation, reagent and alkali were added, the volume made up to a standard and the total iron content determined by the method described above. The results of these tests are given in Table 2.

TABLE 2

Designation of test sample	Iron content in percent	Iron added in percent	Total iron in percent	Iron found
Granulated zinc, tech	0.015	0.008	0.023	0.022
Granulated zinc, Anal. Grade	0.006	0.002	0.008	0.008
Granulated zinc (Kahlbaum) free from arsenic	0.004	0.004	0.008	0.007
Zinc dust, tech.	0.008	0.004	0.012	0.011
Zinc dust, Anal. Grade.	0.006	0.002	0.008	0.008
Zinc dust (Kahlbaum) Anal. Grade	0.006	0.004	0.010	0.010

The colorimetric determination of iron in salts of the alkali and alkaline earth metals

2 g of the salt is weighed into a beaker, dissolved in 10-15 ml of water and 2-3 drops of conc. HNO_3 added to dissolve and oxidize the iron. The solution is quantitatively transferred to a standard 50 ml flask, 2 ml of a 0.25% aqueous solution of protocatechuic aldehyde and 5-6 drops of 10% NaOH are added, the volume made up to the mark with water and carefully mixed.

At the same time 5 ml of the standard iron solution – Solution B– is measured into a 100 ml flask and 4 ml reagent, and 2-3 drops of 10% NaOH added. The volume is made up to the mark with water and shaken thoroughly. The colors of test and blank solution are compared in a Duboscq colorimeter. 0.004% iron can be determined in 2 g of the salts of the alkali and alkaline earth metals. Duplicates are in good agreement.

In order to check on the accuracy of the method experiments were carried out in which salts were used containing a known amount of iron and to these were added a known weight of iron in solution. The total iron was then determined by the colorimetric method described above. The results are given in table 3.

TABLE 3

Designation of test sample	Iron content in percent	Iron added in percent	Total iron in percent	Iron found in percent
Sodium chloride, tech	0.008	0.004	0.012	0.011
Sodium chloride, Anal. grade	0.004	0.002	0.006	0.006
Magnesium chloride, tech.	0.010	0.008	0.018	0.017
Magnesium chloride, Anal. grade	0.004	0.004	0.008	0.008
Calcium chloride, tech.	0.012	0.008	0.020	0.020
Barium chloride, tech.	0.010	0.004	0.014	0.012

The method gives good results. The total iron found in most cases corresponds to the amount taken. The deviations observed in some cases are very small considering the very low iron content.

SUMMARY

1. A new color reaction is proposed for the determination of trivalent iron, which is based on the development of a color on interaction with protocatechuic aldehyde $(OH)_2 \cdot C_6H_3 \cdot CHO$.

The limit of identification in acid media is 0.5 μg Fe in 1 ml solution, and in alkaline media 0.2 μg in 1 ml solution. The majority of the elements at concentrations 3000 times that of the iron do not interfere MoO_4^{2-}, VO_3^-, and Ce^{3+} give the colors with the reagent.

2. It has been established that the color obtained by the interaction of low concentrations of trivalent iron for 25-0.5μg in 1 ml, with protocatechuic-aldehyde in alkaline media conforms to the Lambert-Beer law. On this basis therefore a new colorimetric method for the determination of iron has been worked out.

3. This colorimetric method has been worked out for the determination of iron in metallic aluminum, and zinc, and in the salts of the alkali and alkaline earth metals.

Received December 17, 1949

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THE USE OF DIANTIPYRYLPHENYLMETHANE IN ANALYTICAL CHEMISTRY. 2

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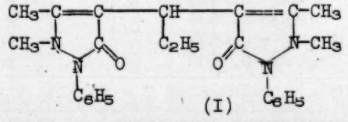
We have shown previously how diantipyrylphenylmethane (I) can be used for the volumetric and gravimetric determination of vanadium:[1]



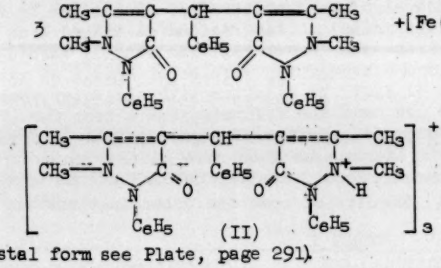
(I)

Further work has demonstrated that diantipyrylphenylmethane under certain conditions gives insoluble or almost insoluble precipitates with the anions $[Fe(CN)_6]^{3-}$, $[Fe(CN)_5\,NO]^{2-}$, $[Co(CN)_6]^{3-}$, and also $Cr_2O_7^{2-}$, $[Co(NO_2)_6]^{3-}$ and some others. In these cases the base (I) reacts with the respective complex acids forming salts of the "ammonia" type with high molecular weights.

In the present article results are given for the quantitative determination of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ by means of diantipyrylphenylmethane, and the compounds formed are described.

Gravimetric Determination Of $[Fe(CN)_6]^{3-}$ With Diantipyrylphenylmethane

When an alcoholic solution of diantipyrylphenylmethane hydrochloride reacts with a solution of $K_3[Fe(CN_6]$ in a weak acid medium, rapid formation of a greenish-yellow crystalline precipitate of the composition $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Fe(CN)_6]\cdot 9H_2O$ occurs according to the following reaction



(II)

(for the crystal form see Plate, page 291)

On heating to 100-120° the compound loses its water of crystalization but not its crystalline structure; the product thus obtained is of a brown color, which clinkers at 138-140° to a black mass.

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1) Gusev, Beiles and Sokolova, The Quantitative Determination of Vanadium by Means of Diantipyrylphenylmethane. J. Anal. Chem. 6, No. 1, p. 43 (1951).

This black mass decomposes with swelling at 155-160°. The compound (II) dissolves in alkalis and strong acids, with gradual separation of diantipyrylphenylmethane; the $[Fe(CN)_6]^{3-}$ ion can be detected in solution; (II) is soluble in 96° alcohol, but precipitates out on addition of water.

For analytical purposes it is essential that the $[Fe(CN)_6]^{4-}$ ion should not react with diantipyrylphenylmethane.

Analysis of the compound prepared (II)

Weight taken, in g	Weight of products obtained, in g	Found percent
0.1016	CO_2—0.2590	C—69.57
0.1120	CO_2—0.2849	C—69.42
0.1016	H_2O—0.0489	H— 5.39
0.1120	H_2O—0.0534	H— 5.31
0.7330	Fe_2O_3—0.0374	Fe- 3.57
0.6960	Fe_2O_3—0.0360	Fe- 3.62

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Fe(CN)_6]$ Calculated C - 69.51%; H - 5.46%; Fe - 3.47%.

Determination of water of crystallization

1.0006 g after drying yielded 0.9082 g.

Found percent: H_2O - 9.23 For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Fe(CN)_6]\cdot 9H_2O$.
calculated percent: H_2O - 9.16.

In the quantitative determination of $[Fe(CN)_6]^{3-}$ it is necessary to carry out the analysis so that towards the end of precipitation the solution contains 50% alcohol, since under these conditions the precipitate of the complex is insoluble while the excess reagent (I) is kept in solution.

The high molecular weight of the compound enables small amounts of $K_3[Fe(CN)_6]$ to be determined.

a. Gravimetric determination of $K_3[Fe(CN)_6]$. To 5 ml of a solution of $K_3[Fe(CN)_6]$ containing 0.025 g of the salt, are added 7 ml water, 3-4 drops of 2 N H_2SO_4 and 12 ml of a 2% alcoholic solution of diantipyrylphenylmethane. A precipitate is immediately formed which after 15 minutes is filtered under vacuum into a sintered glass funnel, the residue is washed from the beaker onto the funnel with filtrate and the precipitate finally washed with 25% aqueous alcohol (10-15 ml) and subsequently with water acidified with nitric acid (4 drops 1 N to 100 ml H_2O). On dilution with the water some diantipyrylphenylmethane separates out from the filtrate, but a test for $[Fe(CN)_6]^{3-}$ by the formation of Turnbull's blue is negative. The precipitate is dried to constant weight at 100-120° for 2 hours; sometimes some clinkering occurs but this does not affect the accuracy of the result. Similar determinations were made with different amounts of $K_3[Fe(CN)_6]$. Results of some the determinations are given in Table 1.

TABLE 1

$K_3[Fe(CN)_6]$ taken		Water, in ml	2% Alcohol solution of (I), in ml	Ppt. (II) obtained, in g	$K_3[Fe(CN)_6]$ found, in g	Expt. error, g
Solution, in ml	Weight, in g					
5	0.0250	7	12	0.1194	0.0245	-0.0005
5	0.0250	7	12	0.1210	0.0248	-0.0002
10	0.0500	15	25	0.2408	0.0494	-0.0006
10	0.0500	15	25	0.2446	0.0520	+0.0020

These results show clearly that the method is applicable to the gravimetric determination of $K_3[Fe(CN)_6]$.

b. The gravimetric determination of $K_3[Fe(CN)_6]$ in the presence of $K_4[Fe(CN)_6]$. To an accurately measured volume of $K_3[Fe(CN)_6]$ of known concentration a solution of $K_4[Fe(CN)_6]$ is added, and the determination carried out by the method described, the amount of water added being decreased by the amount of $K_4[Fe(CN)_6]$ solution used, so that the final solution still contains 50% alcohol.

Results of the determinations are given in table 2.

TABLE 2

$K_3[Fe(CN)_6]$ taken		$K_4[Fe(CN)_6]$ taken		Ppt. II obtained, in g	$K_3[Fe(CN)_6]$ found, in g	Exptl. error, in g
Solution, in ml	Content, in g	Solution, in ml	Content, in g			
5	0.0250	5	0.025	0.1212	0.0248	−0.0002
5	0.0250	5	0.025	0,1210	0.0248	−0.0002
5	0.0250	10	0.05	0.1256	0.0257	+0.0007
5	0.0250	10	0.05	0.1270	0.0260	+0.0010
10	0.0500	10	0.05	0.2456	0.0503	+0.0003
10	0.0500	10	0.05	0.2420	0.0496	−0.0004

c. Gravimetric determination of $K_4[Fe(CN)_6]$. An accurately know volume of $K_4[Fe(CN)_6]$ solution of definite concentration and containing a few drops of 2N H_2SO_4 is oxidized with 0.1 N $KMnO_4$. The $K_3[Fe(CN)_6]$ formed by this oxidation is precipitated with diantipyrylphenylmethane by the method described above.

Results are given in Table 3.

TABLE 3

$K_4[Fe(CN)_6]$ taken		Precipitate (II) obtained, in g	$K_4[Fe(CN)_6]$ found, in g	Experimental error, in g
Solution, in ml	Content, in g			
5	0.0250	0.1080	0.0247	−0.0003
5	0.0250	0.1069	0.0245	−0.0005
10	0.0500	0.2198	0.0504	+0.0004
10	0.0500	0.2610	0.0495	−0.0005

d. Determination of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ when present together. $K_3[Fe(CN)_6]$ is determined in one aliquot as described above and then another aliquot is taken which is preliminarily oxidized with 0.1 N $KMnO_4$ and the total $K_3[Fe(CN)_6]$ determined; $K_4[Fe(CN)_6]$ can then be determined by difference.

Results of these determinations are given in Table 4. For simplification only the total salts expressed as $[Fe(CN)_6]^{3-}$ are given.

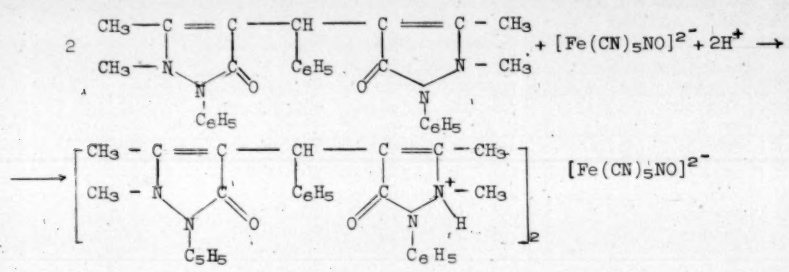
By means of diantipyrylphenylmethane, therefore, it is possible to carry out gravimetric determinations of small amounts of ferro and ferricyanides either separately or together. Attemps at a volumetric method gave high and inconsistent results.

TABLE 4

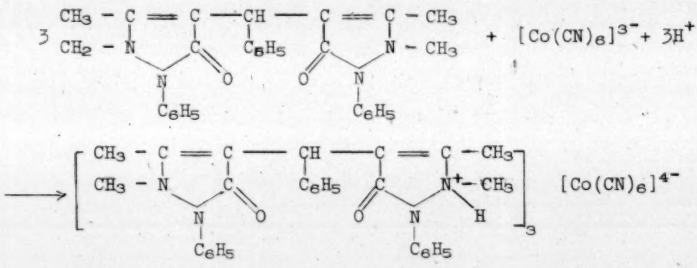
$K_3[Fe(CN)_6]$		$K_4[Fe(CN)_6]$		Ppt. obtained, in g	$[Fe(CN)_6]^{3-}$ found, in g	$[Fe(CN)_6]^{3-}$ calc. theoretical, in g
Solution, in ml	Content, in g	Solution, in ml	Content, in g			
1	0.0050	4	0.0200	0.1134	0.0149	0.0147
1	0.0050	4	0.0200	0.1173	0.0152	0.0147
2	0.0100	5	0.0250	0.1489	0.0201	0.0208
2	0.0100	5	0.0250	0.1467	0.0198	0.0208
3	0.0150	5	0.0250	0.1780	0.0235	0.0241
3	0.0150	5	0.0250	0.1814	0.0239	0.0241
5	0.0250	5	0.0250	0.2420	0.0319	0.0305
5	0.0250	5	0.0250	0.2359	0.0308	0.0305

Interactions Between The Nitroprusside $[Fe(CN)_5NO]^{2-}$ And Cobaltocyanide $[Co(CN)_6]^{3-}$ Anions With Diantipyrylphenylmethane

The reactions between these anions and diantipyrylphenylmethane proceed in the same way as for $[Fe(CN)_6]^{3-}$, i.e., with the formation of " ammonia" salts of the respective acids and base (I):



(III)



(IV)

The reaction between $Na[Fe(CN)_5NO]\cdot 2H_2O$ and diantipyrylphenylmethane (preparation of compound III). To 60 ml of a 2% alcoholic solution of diantipyrylphenylmethane diluted with 40 ml of water, and 0.5 ml of 1 N HCl, is gradually added a solution of 0.2 g nitroprusside in 10 ml water. A white bulky crystalline precipitate forms, which after filtration is washed with 21% aqueous alcohol and dried to constant weight. No $[Fe(CN)_5NO]^{2-}$ anions were detected in the filtrate (acetone test). The compound is a white crystalline material, reminiscent in form of the crystals of complex (II) under the microscope. The complex contains three molecules of water of crystallization. At 180° the anhydrous product decomposes with swelling.

Analysis of the compound formed

Weight taken in g	Weight of products obtained in g	Found Percent
0.1206	CO_2 – 0.2907	C – 65.78
0.1115	CO_2 – 0.2715	C – 65.85
0.1206	H_2O – 0.0555	H – 5.15
0.1115	H_2O – 0.0493	H – 4.90
0.7125	Fe_2O_3 – 0.0478	Fe – 4.69
0.6842	Fe_2O_3 – 0.0465	Fe – 4.75

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2[Fe(CN)_5NO]$. Calculated C –65.96%; H – 5.09%; Fe –4.87%.

0.7964 g was taken for the determination of the water of crystallization 0.7714 g was obtained after drying.

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2H_2[Fe(CN)_5NO]\cdot 3H_2O$. Found percent: H_2O 3.14. Calculated percent: H_2O 3.25.

The reaction between $Na_3[Co(CN)_6]$ and diantipyrylphenylmethane (preparation of compound (IV). To 150 ml of a 1% solution of diantipyrylphenylmethane in 50% aqueous alcohol with 5 drops of 1 N H_2SO_4 is added a weak acid solution of 0.7 g of $Na_3[Co(CN)_6]$ in 25 ml water. The precipitate is washed with 25% aqueous alcohol and dried to constant weight. The complex is white crystals; under the microscope long fine needles are observed. The product contains 14 molecules of water of crystallization, after removal of which by heating, it acquires a rose color.

Analysis of the compound formed

Weight taken, in g	Weight of products obtained, in g		Found Percent	
0.1084	CO_2	0.2749	C	69.21
0.1236	CO_2	0.3132	C	69.14
0.1084	H_2O	0.0514	H	5.31
0.1236	H_2O	0.0592	H	5.36
0.6894	Co_3O_4	0.0337	Co	3.59
0.4604	Co_3O_4	0.0218	Co	3.52

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Co(CN)_6]$. Calculated C - 69.34%, H - 5.44%, Co - 3.66%.

Determination of water of crystallization.

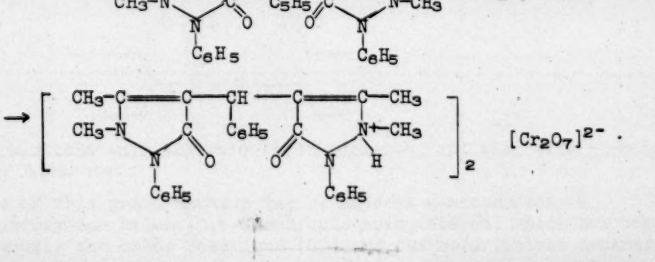
0.2016 g on drying gave 0.1740 anhydrous product.

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Co(CN)_6]\cdot 14H_2O$. Found percent H_2O-13.71. Calculated percent H_2O - 13.5.

A precipitate can be formed by the interaction of diantipyrylphenylmethane with sodium cobaltinitrite $Na_3[Co(NO_2)_6]$. The composition of the complex formed corresponds approximately to the formula $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Co(NO_2)_6]$; it changes with time however.

The Interaction of Diantipyrylphenylmethane with $Cr_2O_7^{2-}$ and CrO_4^{2-} Ions

The formation of well formed crystalline precipitates as the result of the interaction of organic compounds with salts of sexivalent chromium is rare. The reaction therefore between $Cr_2O_7^{2-}$ (or CrO_4^{2-}) and diantipyrylphenylmethane in a weak acid medium is of interest as it leads to the formation of a yellow crystalline precipitate of the composition $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2H_2Cr_2O_7$.



To 100 ml of a 2% solution of diantipyrylphenylmethane in 50% aqueous alcohol is slowly added about 30 ml of a 0.5 N solution of $K_2Cr_2O_7$; yellow crystals separate out, which are filtered off, washed with water and dried in a desiccator. The crystal form is shown in the photograph, Fig. 2. (See Plate, page 291)

This compound easily acquires an orange-red color, particularly if gently heated; at 100° the product is converted into a black sintered mass. The compound is only slightly soluble in water (0.06%), ether (0.02%), but is considerably more soluble in alcohol (0.9%).

Analysis of the compound formed

Wt. taken, in g	Wt. of products obtained, in g	Found percent
0.1938	Cr_2O_3 0.0262	Cr 9.23
0.2474	Cr_2O_3 0.0336	Cr 9.28
0.1278	8.68 ml 0.1 N H_2SO_4	N 9.51
0.1310	8.68 ml 0.1 N H_2SO_4	N 9.28

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2H_2[Cr_2O_7]$. Calculated Cr 9.08%, N 9.55%.

No precipitate is formed by the interaction of diantipyrylphenylmethane with K_2CrO_4. Acidification of the solution with dilute sulfuric acid leads to a slow precipitation of a crystalline precipitate of the same composition as given by $Cr_2O_7^{2-}$.

In conclusion we should like to observe that diantipyrylphenylmethane can form a series of compounds which can find applications in analytical chemistry; e.g., the compound formed with cobalt thiocyanate, with zinc thiocyanate, and others, the investigation of which will be the object of further communications.

At the present time we are studying the possible applications in analytical chemistry of the reaction products of antipyrine with certain aldehydes apart from benzaldehyde, e.g. with salicylaldehyde, paradimethylaminobenzaldehyde, etc.

SUMMARY

1. By the interaction of diantipyrylphenylmethane (I) with $[Fe(CN)_6]^{3-}$, $[Fe(CN)_5NO]^{2-}$, $[Co(CN)_6]^{3-}$ and $[Cr_2O_7]^{2-}$ ions, the compounds (II), (III), (IV) and (V) are formed.

2. A method for the gravimetric determinations of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ ions either separately or together has been worked out.

The determination is made on the basis of a compound of the composition $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Fe(CN)_6]$.

The factor for converting to $[Fe(CN)_6]^{3-}$ is 0.1319.

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A COLOR REACTION FOR THE RARE-EARTH ELEMENTS

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A number of color reactions for the rare-earth elements are either described or mentioned in the literature. Both group reactions and reactions for individual rare-earth elements have been described. Of the group reactions mention may be made of those involving aluminon [16], murexide [1a], pyrogallol or gallic acid [9], and various others.

Color reactions for individual rare-earth elements which have been described are: for cerium – those based on the oxidizing [6,7,15] or chromophoric action of quadrivalent cerium [9, 23,]; for ytterbium – those using the exceptionally strong reducing action of bivalent ytterbium [2]; and for europium the strong reducing action of bivalent europium [3]; for lanthanum – reactions with iodine, acetates and ammonia [5]; for scandium – reactions with o-aminophenylarsinic acid + salicylaldehyde [19] and with murexide [1a].

Wenger and Duckert have published results of their critical study of reagents for cerium [12], rare earths and yttrium [13] and for scandium [14].

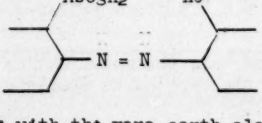
Old methods are still used alongside the new reactions for determination of the rare-earths, e.g., Hildebrand and Lendel in their textbook [17] recommend detection of the rare earths by precipitation as oxalates or fluorides despite the fact that this method is not sensitive enough, and also requires considerable time.

Group reactions for the rare-earths which have been described are only of low selectivity, and convenient methods of elininating interference from other elements have not been worked out for these reactions. Reactions for individual elements are of basic interest for the detection of these elements in their mixtures. These reactions in the majority of cases are complex to carry out, and moreover they are not known for all the rare-earths.

In spite, therefore, of an apparent sufficiency of known reactions, the detection of the rare-earths in minerals and in the presence of other elements still presents difficulties. In this connection, the author considers that the group color reaction for the rare earth elements described in this article may be of interest.

The new color reaction is not selective; however, interference on the part of other elements can be easily eliminated by simple methods which are described, while the confirmatory reaction also described guarantees freedom from errors in making wrong diagnoses on the rare earth elements.

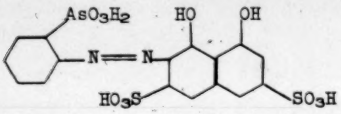
It has been shown previously [18] that compounds which incorporate the atomic grouping:



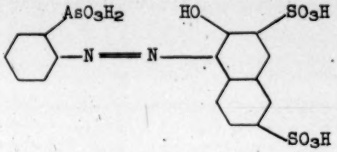
can give color reactions with the rare earth elements, and also with zirconium, thorium, and other elements.

Of reagents of this group mention may be made of o-arsonobenzene <1-azo-2> -2-hydroxynaphthalene-3,6-disulfonic acid (thoron) which has been recommended prevously for color reactions [20] and the colorimetric determination

of thorium [11,25] and of o-arsonobenzene- ⟨1-azo-2⟩ - 1,8 dihydroxynaphthalene-3,6-disulfonic acid which we shall call arsenazo: [1]



Arsenazo



Thoron

In the present article we shall describe a color reaction with arsenazo.

Mechanism of the color reaction. A cylic complex salt is formed during reaction with arsenazo in which there is sufficient intramolecular dissociation for determining the color observed [21].

The ionic state of the reagent which exists in solutions of this reagent in concentrated sulfuric acid ("azo-salt" - blue-violet color) and the ionic state which exists in alkaline solutions (phenolates - bluish-rose color) participate in the red-violet color of the solutions of complexes of the rare earth elements with arsenazo.

The Color Reactions of the Reagent Arsenazo

Solutions of arsenazo alone in neutral and in weak acid solutions are of a rose color, while in alkaline solution they are bluish-rose.

The rare-earth elements, Sc and Y form reddish-violet colors in neutral media. Under these conditions the following elements also give color reactions:

U^{VI} - blue coloration
Cu^{II} - blue-violet coloration
Al, V^{IV}, Th[18] - violet coloration or precipitate
Zr^{IV}, Ga, In, Pd^{II} - bluish-rose coloration or precipitate
Fe^{III} - brown lilac coloration

In addition large amounts of Ti^{IV} and Cr^{III} give violet precipitates particularly on heating. Nb and Ta also give violet precipitates under different conditions (arsenazo is added to an alkaline solution of niobates or tantalates and the mixture subsequently acidified).

Detection of the Rare Earth Elements in Pure Solutions and a Confirmatory Reaction

The rare earth elements form red-violet colors only in a neutral medium. In acid and even in weakly acid solutions no reaction occurs.

The optimum pH is ca. 7.2 (bluish-green for bromothymol blue), but reactions can be carried out in the pH range 6.5-7.5 (from yellow-green to greenish-blue for bromothymol blue).

Since the substances introduced into the usual buffer solutions in order to get the requisite pH values mask the rare earth elements, the optimum pH is produced by means of urotropine.

Detection is carried out as follows.

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[1] The synthesis of arsenazo is described at the end of this article. The synthesis of thoron has been described in [20] and in addition is included in Kulberg's book [24].

To 2 ml of test solution with an acidity no greater than 0.05 N HCl are added 1-2 drops of a 0.05% aqueous solution of arsenazo. If the solution is neutral then it is necessary to acidify it before addition of arsenazo by addition of 5 drops of 0.1 N HCl.

The absence of any change in the rose color of the reagent indicates the absence of iron, zirconium and thorium.

Next 5-10 drops of a 25% solution of urotropine are added. If only 5 μg of a rare earth element is present a red-violet color develops, which immediately changes to a rose color on addition of a few drops of 1% sodium phosphate solution. (Confirmatory test, distinction from Al, Cu, V^{IV}, Zr and partially from Th).

This slow disappearance of color after addition of sodium phosphate is characteristic for the rare-earth elements. The colors formed by other elements either do not change as a result of adding phosphate or only change slowly. If more than 5μg of a rare-earth element is present a greater amount of arsenazo can be used to increase the definition of the reaction.
For detection of the rare-earth elements in very dilute solutions it is necessary to establish the required pH value more accurately.

This is done as follows. The neutral or weak acid test solution is divided into two, to one half is added bromothymol blue and then simultaneously and equal number of drops of a 25% solution of urotropine is added to both halves until the half with the bromothymol blue acquires a bluish-green color. At this point addition of urotropine is stopped and the arsenazo is added to the half free from bromothymol blue. At high dilutions it is necessary to compare with the color of a blank.

The limiting dilution is greater than 1:3,000,000. When the optimum pH value is very carefully prepared it is possible to go as low as 1:5,000,000, but the sensitivity falls off sharply for even small deviations from the optimum pH.

The limit of identification is 0.4μg of a rare earth element (in 1 ml at a dilution of 1:2,500,000)

Fluorides, phosphates, tungstates, oxalates, citrates, tartrates, and other complex-forming compounds interfere with the color reaction because they form weakly dissociated complexes with the rare earth elements. Salicylates exhibit a slight effect.

In order to carry out the reaction by a drop technique, a drop of 0.2-0.3% solution of arsenazo is placed on filter paper and dried. The stain is touched with the end of a very fine hair capillary with a diameter of 0.2 mm and a micro drop of the test solution with the requisite pH value slowly allowed to form.

If rare-earth elements are present, then at the point of contact a violet or blue spot with diffuse edges is formed; in the absence of rare earth elements as a result of washing out of the reagent - a white spot is formed.

The limiting dilution is 1:30,000.

The limit of identification is 0.03μg of a rare earth element (in a 0.001 ml microdrop at a dilution of 30,000).

It must be emphasized that in carrying out the reaction by a drop technique, the sensitivity is very strongly dependent on the method employed. The sensitivity is greater the finer the end of the capillary and the slower the microdrop is allowed to form.

Detection of Rare-Earth Elements in the Presence of Other Elements

The direct detection of rare-earth elements is possible without any auxiliary procedures in the presence of considerable amounts of the following elements: Li, K, Na, NH_4^+: Ag, Ca, Sr, Ba, Mg, Zn, Cd, Hg^{II}, Sn^{IV}, Pb, V^V, Mo, Co, Ni and also in the presence of all anions which do not mask the rare earth elements (Cl^-, Br^-, I^-, ClO_4^-, SO_4^{2-}, $S_2O_3^{2-}$, NO_3^-). Phosphates, pyrophosphates, fluorides and tungstates mask the rare-earth elements and the reaction is not possible when these are present.

By adopting special masking methods, the rare-earth elements can be detected even in the presence of certain elements which themselves give a color reaction. Thus the detection of the rare-earth elements is possible in the presence of:

Al, Cu – on addition of salicylates
Cu – " " " $Na_2S_2O_3$
U – " " " H_2O_2

Detection of the Rare-Earth Elements in the Presence of Iron

The color reaction does not work in the presence of iron Fe^{III}. If iron is present in amounts of only 10-15 times that of the rare earth elements, detection is still possible after reduction of Fe^{III} to Fe^{II} by ascorbic acid. But in this case the color formed is of a different shade and quickly disappears, since under these conditions the Fe^{II} reaction leads to a break down of the reagent.

Small amounts of iron up to one milligram can be conveniently removed by extraction in the form of the 8-hydroxyquinolate. At the same time small amounts of aluminum are removed. This separation is effected as follows.

2-3 ml of the neutral test solutions are acidified with 4-5 drops of 0.1 N HCl and 1-2 drops of a 0.05% solution of arsenazo introduced. The mixture is shaken with 2 ml of a 1% solution of 8-hydroxyquinoline in benzene. Pure benzene may be used and a small crystal of 8-hydroxyquinoline added to it in a test tube.

The extracted iron colors the benzene a dirty green color. If the color formed is too intense, the upper benzene layer is removed with a capillary fitted with a rubber bulb and the extraction repeated with a fresh portion of a benzene solution of 8-hydroxyquinoline. When the color finally developed is not too intense, the benzene layer is removed, fresh benzene is added, and 6-8 drops of a 25% solution of urotropine added to the test solution, and the mixture shaken after the addition of each drop. When 1-2 drops have been added it is useful to remove the benzene layer and replace it with fresh. The benzene layer is carefully removed with a capillary and the lower aqueous layer is washed a few times with pure benzene, the benzene being removed after each wash. This procedure is repeated until the benzene remains completely colorless.

In the presence of rare earth elements the lower aqueous layer is colored violet but this changes instantly to a rose color on addition of sodium phosphate.

By this method it is possible to determine 1-2 μg of a rare earth element in 2 ml for a Fe^{III} content of 50 μg and 30 μg aluminum in the original solution.

It is more convenient to remove large amounts of iron by extraction with amylacetate [21] and not with 8-hydroxyquinoline or the method using stannic chloride described below. The procedure is as follows.

The test solution is evaporated to dryness in a test tube. If the test tube is heated on a gas burner, it should be shaken to prevent the contents spluttering, and in order to facilitate removal of condensed vapor on the sides of the test tube, air can be blown into the tube by means of a bent tube at intervals.

The residue is dissolved in 1-2 ml of HCl, Sp. gr. 1.18-1.19, 1-2 ml amylacetate is added, and the mixture shaken vigorously. The upper yellow layer containing the extracted iron is carefully removed with a capillary. If the lower acid layer has an appreciable yellow color, the extraction is repeated with fresh portions of amylacetate. For an amount of iron 100 times more than the rare earth elements one extraction is sufficient.

The acid residue is transferred to a small beaker and evaporated to dryness on a water bath. The residue is dissolved in water and the reaction for the rare-earth elements carried out as described above, separating, if necessary the remaining traces of iron and aluminum by extraction with 8-hydroxyquinoline.

Separation of the Rare-Earth Elements from Other Elements

If the amount of the interfering elements – titanium, zirconium, thorium – is not too great in comparison with the amount of rare-earth elements present, the easily hydrolyzable cations of all these elements can be removed simultaneously by co-precipitation with stannic acid, which is precipitated on hydrolysis of $SnCl_4$. This method is included below in the description of the method of detecting rare earth elements in minerals. Iron is also precipitated with stannic acid, but aluminum is not.

The Colorimetric Determination of the Rare-Earth Elements

The reaction described is also suitable for the quantitative colorimetric determination of the rare earth elements in pure solutions or in the presence of non-interfering elements. The scale method may be used (standard series method). Or the method of colorimetric titration, since the color develops slowly.

In the test solution the reagent should of course be in excess of the rare earth elements. Therefore the solution to be determined colorimetrically should have a red-violet (violet + rose) and not a violet color.

Since the individual rare earth elements for identical pH values give somewhat different colors, the individual rare earth elements in the standard solutions should be in the same proportions as in the test sample. When working with pure individual elements these complications do not apply.

As an example we describe the determination of neodymium. 3 ml of the test solution containing 1-10 μg of neodymium is introduced into a test tube and 0.2 ml of 0.1 N HCl and 0.2 ml of a 25% solution of urotropine added. A 0.01% aqueous solution of arsenazo is then added from a microburette until the violet color which is first formed changes into a distinct red-violet color. Into a second test tube exactly the same amount of arsenazo is introduced from the microburette, (important) and a volume of water slightly less than that of the test solution, the same amount of HCl and urotorpine respectively also added. This mixture is titrated with a standard solution of neodymium containing 10 μg/ml Nd from a microburette until the color obtained is the same as that of the solution in the first test tube. The volumes of the solutions are then equalized with water.

This procedure for the colorimetric determination of rare earth elements is carried out more quickly than the method recommended in the literature, according to which the rare-earth element is first precipitated as a phosphate and the phosphorus then determined colorimetrically by the molybdate method [1].

Detection of Rare Earth Elements in Minerals

Since the greatest difficulties encountered are those arising from the presence of large amounts of aluminum, it is recommended that the test object be freed mechanically as much as possible from the minerals rich in aluminum. This procedure is however not compulsory, since the confirmatory test with sodium phosphate ensures freedom from detecting a rare earth element where it does not occur.

Procedure. A grain of the mineral from 1-10 mg in weight is carefully crushed in an agate mortar, mixed with sodium carbonate, and portions fused either on the

loop of a platinum wire or on the lid of a platinum crucible. The melt is dissolved in water acidified with HCl, and a few more drops HCl added and the solution evaporated almost to dryness.

The residue is either diluted with HCl, Sp. gr. 1.18-1.19, or with water, according to whether or not it is proposed to use amylacetate for extraction of the iron. If an extraction is performed the residue is diluted with water after almost complete evaporation of the HCl on the water bath.

The amount of water taken should be such that the concentration of aluminum is not more than ca. 0.15 μg/ml of the element. By addition, if necessary, of a sodium bicarbonate solution, the solution is made slightly acid to congo red (incomplete blueing of congo red paper). 1-2 drops of a 60% aqueous solution of $SnCl_4$ are then added, and the mixture heated to boiling, and filtered from the precipitated meta-stannic acid.

If all the thorium has been completely removed, on addition to part of the filtrate of a drop of the arsenazo solution no violet color should develop; if thorium is present the separation with $SnCl_4$ is repeated in a less acid solution. When small amounts of the rare earth elements are present, the filtrate is either neutralized with ammonia or left weakly acid.

To 2 ml of the filtrate are added 1-2 drops of a 0.05% solution of arsenazo followed by 8 drops of ammonium salicylate[1] solution and 1-1.5 ml of a 25% solution of urotropine.

If rare-earth elements are present a red-violet color developes which slowly changes to a rose color on addition of a few drops of 1% $Na_2HPO_4 \cdot 12H_2O$. In the absence of rare-earth elements the test remains a rose color.

When detecting very small amounts of the rare earth elements it is useful to split the solution obtained between two test tubes and to add sodium phosphate to one and compare the color shades thus obtained.

In the presence of uranium, blue solutions are formed. In this case the blue color can be destroyed by addition of H_2O_2, taking care not to add excess.

The limiting dilution of the rare-earth elements calculated as oxides in the filtrate from (meta)-stannic acid is 1:800,000. The limiting ratio

$$(\text{rare earth})_2O_3 : Al_2O_3 = 1 : 170.$$

Particles of monazite or orthite which are practically invisible to the naked eye give a definite reaction for rare-earth elements.

Synthesis of Arsenazo - o-Arsonobenzene-<1-azo-2>-1,8-dihydroxynaphthalene-3,6-disulfonic acid (sodium salt)

2.17 g of o-aminophenylarsonic acid (0.01 mol) is dissolved in 40 ml water and 3 ml HCl, sp gr. 1.12, added. The mixture is cooled and then diazotized by addition of 5 ml of 2N $NaNO_2$. The solution of the diazo compound is filtered off and poured into a cooled, filtered, solution of 4.3 g pure chromotropic acid (free from H-acid) and 4 g anhdyrous sodium carbonate in 20 ml water. After standing for 2 hours an excess of HCl, sp. gr. 1.19, is added and the dark red-brown precipitate filtered off, washed with 3 ml of HCl, sp. gr. 1.12, and recrystallized from a small volume of water. It is air dried. Yield of recrystallized product is ca. 4 g of a dark red powder.

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[1] 10 g salicylic acid is shaken up with 50 ml of water and carefully neutralized with ammonia and the solution made up to 100 ml with water.

The o-aminophenylarsonic acid necessary for the above synthesis is obtained by reduction of o-nitrophenylarsonic acid by $FeSO_4$ (or better $FeCl_2$)++ NaOH [4]. o-Nitrophenylarsonic acid is prepared by Barth's reaction from diazotized o-nitraniline and alkaline arsenite solution [10].

SUMMARY

The reagent arsenazo (o-arsonobenzene-<1-azo-2>-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Na-salt) dissolves in water giving a rose colored solution. With rare earth elements in neutral solution arsenazo forms red-violet colors which enable these elements to be detected at dilutions down to 1 : 3,000,000.

The detection of the rare earth elements in their pure solutions is described together with methods for eliminating interference from iron and other elements which react with arsenazo.

A method is described for detecting the rare earth elements in minerals, in which part of the interfering elements are separated by coprecipitation with precipitated meta stannic acid formed by the hydrolysis of $SnCl_4$, while any interfering elements remaining in solution are masked by means of ammonium salicylate.

The synthesis of the reagent is described.

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DETECTION OF CERTAIN RARE EARTH ELEMENTS WHEN PRESENT TOGETHER

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The close similarity between the chemical properties of the rare-earth elements is known to be a result of the identical structure of the two outer electron shells. An atom of one of the rare-earth elements differs from an atom of another only in the number of electrons in the 4f level. As a result up to the present characteristic reactions for the detection of the ions of individual rare-earth elements have been practically unknown. More or less specific reactions have only been described for ions of cerium, lanthanum and europium [1]. In this connection therefore a search for chemical methods for the detection of individual rare-earth elements in the presence of others is extremely desirable and of very great practical importance. The considerable experience which has been accumulated on this question, although not yielding any positive results, has led to the conclusion that the normal methods of qualitative analysis cannot be effective in the analytical chemistry of the rare earth elements.

The method proposed by us consists in converting the test compounds of the rare-earth elements into oxides and studying the interactions of these oxides with solutions of specially selected reagents. This leads to a considerable increase in the specificity, since the properties of the ions of the rare-earth elements are usually more like each other than the properties of their compounds of the same type (e.g. compare the ions of Nd^{3+} and La^{3+} and the oxides Nd_2O_3 and La_2O_3; the oxides differ essentially from each other in their basicity). In addition the possibility arises of using, for analytical purposes, compounds containing the rare-earth elements in valency states which in practice do not exist in solution (e.g. the higher oxides of praseodymium).

Detection of Lanthanum in the Presence of Other Rare Earth Elements and Other Elements Similar To It

On calcining, the carbonates, oxalates, and nitrates of other rare-earth elements and also of yttrium and thorium form oxides with weak acid properties and the two elements nearest to lanthanum – cerium and praseodymium – behave similarly. lanthanum is the only element which forms a strongly basic oxide, La_2O_3. Experiment shows that indicators with a transition interval in the pH range 6.4-10, change their colors sharply in the presence of La_2O_3, but remain practically unchanged in the presence of the oxides of other rare-earth elements. The most suitable indicator is phenolsulfophthalein (phenol-red) with a transition pH interval at 6.4-9. The yellow color of the indicator changes to a bright red in the presence of La_2O_3. This indicator enables 0.1 g of La (III) (after evaporation of 0.1 ml of a solution of lanthanum nitrate with subsequent calcining) to be detected at a limiting dilution of 1:1,000,000. This method under the experimental conditions used is strictly specific and enables lanthanum to be detected in the presence of cerium, praseodymium, neodymium, thorium, scandium and yttrium for a ratio of La:Me of 1:10,000 where Me is Ce, Pr, Nd. In the detection of small amounts of lanthanum in the presence of excess neodymium it is necessary to remember that neodymium oxide, after a period of 1-2 minutes, colors the reaction solution

an orange-rose color. In this case, therefore, 1-3 drops of acetone are added. If only 0.01% of lanthanum is present the color persists. In the absence of lanthanum (or when the amount of lanthanum is less than 0.01%) the color changes to the initial yellow. The role of acetone consists in lowering the sensitivity of the reagent to hydroxyl ions [4]. Only strong bases such as magnesium oxide and calcium oxide interfere with the reaction.

Procedure

Preparation of Reagent. 10 mg of phenol red is dissolved in 2 ml warm alcohol and 8 ml water added. The solution is stable.

The reaction. A few milligrams of the test sample or mixture of rare-earth salts (nitrates, oxalates, carbonates, double-ammonium nitrate salts, oxides, etc.) are placed on a platinum spoon or microbeaker and calcined in the flame of a gas burner for 1-2 minutes at a temperature of ca. 800° (when testing a solution it is preliminarily carefully evaporated). After cooling, the oxides which remain are transferred to one of the depressions on a porcelain drop test plate (for small amounts of test sample the reaction can be carried out directly in the vessel in which calcining is carried out) and a drop of the reagent added and mixed with a glass rod. If lanthanum is present, the yellow color of the reagent immediately turns red or rose. In doubtful cases 2-3 drops of acetone are added and mixed in. If no lanthanum is present the solution becomes yellow again. If a large amount of praseodymium is present it is convenient to make observation by means of a magnifying glass.

Detection of Cerium in the Presence of Other Rare Earth Elements and of Thorium Oxide

The reaction which we propose for cerium is based on the oxidation of phenylanthranilic acid, which is used in cerimetry as an oxidation-reduction indicator [5], by cerium dioxide. According to our observations it is possible to detect 0.001 μg of Ce (IV) at a limiting dilution of 1:1,000,000 by the appearance of a violet color. Since calcined cerium dioxide reacts sufficiently rapidly with the reagent, it seems to be a very suitable method for detecting traces of cerium. This reaction enables 0.001% CeO_2 to be detected in thorium oxide and also in the oxides of neodymium, lanthanum, and in other rare earth elements. The detection of cerium in the presence of praseodymium presents some difficulties, since salts of praseodymium decompose on calcining, forming higher oxides, chiefly PrO_2. The latter is a strong oxidizing agent like CeO_2 but though it does not oxidize phenylanthranilic acid as rapidly as CeO_2 it still interferes with the detection of cerium. This interference on the part of PrO_2 can be easily eliminated, if before the test the mixture of oxides is heated slightly with dilute sufuric acid when the PrO_2 forms $Pr_2(SO_4)_3$ while CeO_2 remains unchanged; in this way 0.001% of cerium can be detected in praseodymium preparations.

This reaction for Ce is characterized not only by a considerable sensitivity but also by its high specificity. Only strong oxidizing agents which are capable of oxidizing phenylanthranilic acid in a sulfuric acid medium interfere with the reaction.

Procedure

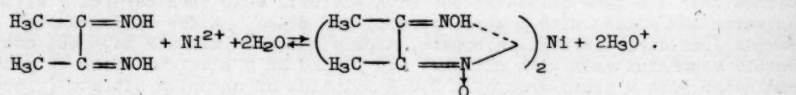
Preparation of reagent. 6 mg of phenylanthranilic acid is dissolved in 10 ml of a 0.1% solution of sodium carbonate.

The reaction. Thorium oxide and the oxides of the rare earth elements (with the exception of preparations containing praseodymium) are tested directly. Carbonates, oxalates, nitrates, double ammonium and magnesium nitrate salts are tested after preliminary calcining in a platinum spoon or in a micro beaker in the flame of a gas burner for 1-2 minutes at ca. 800°. On cooling, a few grains of the oxides formed (for testing a fraction of a milligram is enough) are placed in one of the depressions on a drop test plate, where 4 drops of H_2SO_4 (% = 1.84)

and a drop of phenylanthranilic acid solution have been placed beforehand. Immediately after mixing or 1-2 minutes afterwards, a violet color develops. If praseodymium is present, 1-2 drops of H_2SO_4 are added to the almost cooled, calcined oxides on the platinum spoon (on which calcining is carried out) and the mixture slightly warmed. The reaction between PrO_2 and H_2SO_4 is very rapid and its completion is established by the disappearance of the original black or dark color of the oxides. After this treatment the contents of the spoon are transferred to one of the depressions on the drop test plate and the procedure described above subsequently followed.

Detection of Neodymium in the Presence of Praseodymium and Derium

When the nitrates, oxalates and carbonates of cerium, praseodymium and neodymium are calcined, CeO_2, PrO_2 and Nd_2O_3 respectively are formed of which only Nd_2O_3 possesses any appreciable basic properties. This can serve as a basis for developing a method of detecting neodymium in the presence of praseodymium and cerium by means of the equilibrium solution formed by the interaction of dimethylglyoxime with a nickel salt in a neutral medium.



Feigl [6] showed that this solution is an unusually sensitive reagent for compounds possessing basic properties; in the presence of basic compounds a red precipitate of nickel dimethylglyoxime is formed as a result of the neutralization or adsorption of the hydroxonium ions and subsequent displacement of the equilibrium to the right. The low solubility of the substance with basic properties does not hinder the course of the reaction. Neodymium oxide reacts immediately on contact with the equilibrium solution with the formation of nickel dimethylglyoxime. Praseodymium dioxide reacts with the equilibrium solutions very slowly and it is only after 7-10 minutes that the first signs of a reaction begin to appear. Since the praseodymium compound at our disposal contains traces of neodymium (spectrographic analysis) we could not decide conclusively whether the slow appearance of the effect of the reaction is the result of the presence of these traces of neodymium or whether in fact there is a slow reaction between PrO_2 and the equilibrium solution. CeO_2 does not react with the equilibrium solution even on standing for many hours.

TABLE 1

Time necessary for the appearance of a color on the interaction of the reagent with praseodymium dioxide containing traces of neodymium oxide

Content of nedoymium in the praseodymium compound in percent	Time for color to appear in minutes
10-3	a few seconds
1	0.5
0.1	2
0.01	3
Control (praseodymium containing traces of neodymium)	7 (more clearly 15)

The sensitivity of this reaction is very high—even a grain of Nd_2O_3 practically invisible to the naked eye gives an immediate positive reaction. It is possible to detect 0.01% neodymium in preparations of cerium or praseodymium by this method. The rate at which the red nickel dimethylglyoxime appears, up to

a certain extent characterizes the quantity of neodymium in praseodymium preparations (Table 1).

It is obvious that the reaction just described is reliable only in the absence of materials of a basic character. Lanthanum oxide and the oxides of the rare earth elements up to Er_2O_3 interfere.

The succesful use of this reaction depends on scrupulous accuracy since even traces of compounds of a basic character give rise to a positive reaction.

Procedure

Preparation of reagent. 10 ml of a 4% solution of nickel nitrate is mixed with 20 ml of a 1% alcoholic solution of dimethylglyoxime, heated for 5 minutes on a water bath and filtered. In well covered flasks of inert glass the reagent keeps for 1-2 weeks. If a precipitate forms during storage it should be filtered off.

Reaction. The reaction is carried out in special micro tubes made from inert glass (or pyrex) and fitted with a ground glass stopper, (see diagram). Before test the tube is washed out with sulfuric acid then carefully with distilled water and rinsed with neutral alcohol and dried. A few milligrams of the test sample (oxalate, nitrate, carbonate, double ammonium nitrate salt but not the double magnesium salt with nitrate) are placed on a platinum spoon or microbeaker and mixed with a micro-drop of a 0.01% solution of chromium nitrate (traces of chromium according to Ryabchikov and Terentev [7] help the complete conversion of praseodymium to the higher oxides). The test sample is at first carefully and then more strongly heated in the flame of a gas burner with a blowpipe or jet (ca. 800° but not more than 900°). After cooling the oxides obtained are transferred by means of a micro funnel into the micro test tube to which 3-5 drops of reagent are added by means of a capillary. The ground glass stopper is inserted and observation made of any changes which occur, the tube being periodically shaken. Observations are made with a magnifying glass with a magnification of 5-10. The appearance of rose crystals after an interval of not more than 3 minutes, directly on the surface of the solid phase and also floating on the liquid indicates the presence of neodymium in the test sample of praseodymium or cerium (when other compounds of a basic character are know to be absent).

4/5 actual size

When preparations of cerium or praseodymium thoroughly purified from foreign materials are tested, as a rule one need not be apprehensive of mistakes connected with the presence of the substances indicated (i.e. compounds of a basic character).

Detection of Praseodymium in the Presence of Neodymium, Cerium, and Other Rare Earth Elements

The black product formed on calcining the nitrate or oxalate of praseodymium [8] according to some results corresponds to the empirical formula Pr_6O_{11}, while according to others [9] it corresponds to PrO_2. In contrast to CeO_2, this black product is fairly soluble in acids forming the respective salts of trivalent praseodymium. The nitrate and oxalate of neodymium on calcining in air form the normal oxide Nd_2O_3. The existence of the higher oxide of neodymium NdO_2 which apparently is formed on calcining of the oxalate in an oxygen atmosphere is doubtful [9].

The oxidation-reduction potential of the system:

$$Pr(III) - \underline{e} \rightleftarrows Pr(IV)$$

is greater than 1.6 V [10].

Thus it seems possible [11] that an oxidation-reduction reaction can be used for detecting praseodymium (after conversion of the higher oxides) in the presence of neodymium.

Of a number of oraganic compounds which we have tested the most suitable as reagents for Pr(IV) were benzidene and particularly o-tolidine, which on oxidation form blue compounds [12].

If an acetic acid solution of o-tolidine is allowed to act on the higher oxides of praseodymium formed by calcining the oxalate, nitrate, or carbonate, an intense light blue or dark blue color is immediately formed, which is the result of the formation of tolidine blue. The limit of identification is 0.0 μg of Pr at a limiting dilution of 1:10,000,000.

A spectrographically pure preparation of magnesium neodymium nitrate gives a scarcely observable color (less intense than that for 0.01 μg of Pr). Neodymium preparations containing praseodymium give intense positive reactions. Thus it is possible to detect in an aliquot of magnesium neodymium nitrate containing 5 mg neodymium as little as 0.04 μg of praseodymium, corresponding to a ratio of Nd:Pr = 1:12,500.

Calcined CeO_2 when reacted with a solution of o-tolidine in acetic acid gives only a pale blue color, while the color of the solution above the precipitate remains practically unchanged (acquires a pale-greenish color). This fact, coupled with the insolubility of CeO_2 in acetic acid, enables traces of praseodymium to be detected in the presence of cerium. Thus the spectrographically pure preparation of magnesium cerium nitrate at our disposal showed a negative reaction for praseodymium, while that containing traces of praseodymium gave a definite reaction.

Ions which under the reaction conditions form higher oxides capable of dissolving in acetic acid and in such a solution oxidizing the o-tolidine, interfere with the detection of praseodymium.

Of the other rare earth elements only terbium is capable of giving a similar reaction, since its compounds on calcining form Tb_4O_7, in which terbium is found partially in the quadrivalent state. Nevertheless Tb_4O_7 in contrast to PrO_2 at elevated temperatures is unstable and completely decomposes at 800° in a nitrogen atmosphere, being converted into colorless Tb_2O_3 [9]. Unfortunately we did not have any terbium compound at our disposal so that we coule not test its effect on the reaction which we have suggested for praseodymium.

Procedure

Preparation of reagent. 0.02 g of o-tolidine is dissolved in 1 ml 60% acetic acid by slight heating and 2 ml of 1 N sodium acetate added. If any turbidity develops a few drops of acetone are added to clarify the solution. The reagent is stable and should not acquire a blue color on storing in a stoppered dark flask.

The reaction. The reaction can be carried out with either the dry test mixture - oxalates, nitrates, carbonates, the double ammonium and magnesium salts, or with their solutions. A few milligrams of the dry mixture or a corresponding number of drops of the test solution are placed in a platinum spoon or microbeaker and at first carefully heated, then in the course of 0.5-1 minute the mixture is calcined at a red heat in the flame of a gas burner (temperature of 800° but not more 900°). After cooling 2-3 drops of reagent solution are placed on the spoon. If praseodymium is present then a more or less intensive blue or pale blue color develops both on the liquid and solid phase either immediately or within a few seconds. If the test sample of cerium or neodymium does not contain praseodymium, then only the solid phase is colored blue, while the liquid above the solid remains colorless or has a hardly observable greenish color. A blank test with distilled water or with spectrographically pure preparations of the rare earth elements is essential only when a very pale blue color is obtained, indicating vanishingly small amounts of praseodymium in the test sample.

SUMMARY

A method has been developed for the detection of lanthanum, cerium, and praseodymium in the presence of other rare earth elements, and the detection of neodymium in the presence of praseodymium and cerium. Phenol red is the reagent used to detect lanthanum, phenylanthranilic acid for cerium, and equilibrium solution of nickel dimethylglyoxime for neodymium, and o-tolidine for praseodymium.

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THE REACTION BETWEEN THE BISMUTH ION AND BENZIDENE

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Benzidene, which was synthesized by N.N.Zinnin in 1845, has been widely used during the last 50 years both in analytical chemistry and also for the syntheses of dyes [1] and a number of other compounds.

Feigl [2] by means of benzidene detected the ions of Cu, Pb, Au, Cr, Mn, Tl, Ce, F, CN, CNS, S_2O_8, SiO_4, and Tananaev [3] in addition detected $[SiF_6]^-$, NO_2^- and Cl^- ions.

The capacity of benzidene to give with certain acids very slightly soluble salts has been adopted for the determination of sulfuric [4], tungstic [5], and phosphoric acids [6], respectively.

In 1930, Tugarinov [7], while studying the possibility of using organic reagents for the qualitative detection of cations, briefly described a reaction between bismuth salts, benzidene and potassium iodide. The absence in the work mentioned of any detailed results characterizing the compound formed prompted us to attempt to fill this gap.

When a crystal of potassium iodide is added to a clear and not very dilute solution of a bismuth salt until the precipitate originally formed dissolves, then as a result of the formation of $[BiI_4]^-$ ions the liquid acquires a bright yellow color. Greater amounts of potassium iodide lead to the formation of $[BiI_5]^{2-}$ ions and the appearance of an orange-yellow color. On addition of a solution of benzidene hydrochloride to the liquid thus obtained, a golden-yellow or bright red precipitate forms immediately. If liquid and precipitate are heated to a temperature not exceeding 75° the golden-yellow crystals dissolve and bright red crystals settle out on cooling. Increasing the acid concentration favors the reverse process, but in the presence of concentrated acid the reaction ceases altogether. Use of a microscope facilitates the detection of bismuth in small amounts of liquid. In a drop of 0.01 N $Bi(NO_3)_3$ in the cold, golden-yellow crystals, of irregular, needle-like form, appear after 1-3 minutes, while in a drop of 0.004 $Bi(NO_3)_3$ containing 0.014 mg of the Bi ion, crystals can be observed after 3-5 minutes.

The crystals may have different forms. During rapid crystalization from a hot solution, bright red rhombohedra are formed, which in time dissolve and are replaced by more or less regularly shaped parallellepiped and needles (Fig. 1; see plate, page 291) . Slow crystallization leads to the formation of irregular needle-shaped crystals (Fig. 2, Plate). Under favorable condition of growth their length attains 1 cm.

For the study of the properties and composition of these crystals they were prepared as follows: to a clear, concentrated solution of bismuth chloride was added crystalline potassium iodide until an orange-yellow color was formed. To the clear liquid thus prepared was added a solution of benzidene hydrochloride (excess of the latter should be avoided). The liquid and precipitate which was formed were heated on a water bath to a temperature not greater than 75°. If the transition of the yellow crystals into the red is not fast enough, then an

additional amount of potassium iodide can be added. On rapid cooling of the heated solution by means of cold water, fine crystals separated out, which, after removal from the liquid, were dried between sheets of filter paper. If crystals of benzidene are detected in the preparation the precipitate is recrystallized under the same conditions of temperature in a small volume of liquid containing the $[BiI_5]^{2-}$ ion. If the air-dried crystals are allowed to stand for a long time in the open in bright sunlight there occurs a gradual change in the color to a chocolate brown. This same brown color also develops with time if the crystals are exposed to the ultraviolet from a quartz lamp. The color of the precipitate underneath the surface of the mother liquor or the color of the dry precipitate in a closed vessel in the dark does not change in the course of many months.

No solvent has been found for the precipitate. It is completely insoluble in hot and cold water, ethyl alcohol, chloroform, carbon tetrachloride and acetone. It hydrolyzes in water.

Concentrated acids and alkalis rapidly destroy the red crystals. Hydrochloric acid favors a change of the color of the crystals to yellow. Concentrated nitric acid at first preserves the external form of the crystals, but changes their color initially to black, which eventually changes to brown. At the same time elemental iodine is formed. Hot nitric acid causes a rapid break down of the substance, with simultaneous separation of violet iodine fumes. Concentrated sulfuric acid destroys the substance, with the formation of a dark powdery mass and colorless tablets of benzidene sulfate. The action of caustic alkalis forms a white amorphous precipitate, while aqueous ammonia gives a yellow precipitate. Gaseous ammonia slowly changes the red color of the crystals to a lemon-yellow.

Elevated temperatures have the following effects: above 78° the crystals gradually begin to loose their bright red color and acquire a brown color, which in its turn becomes chocolate brown. Intensive decomposition sets in at 241°. Crystals dried at 150-190° on slow cooling absorb moisture from the air and regain their original red color. This type of change can be repeated several times on one lot of crystals. On moistening freshly dried crystals by breathing on them, it is possible to observe the restoration of the original bright red color in the course of a few minutes.

The air dried powder was analyzed to determine its composition. Iodine was determined as follows: 0.15–0.25 g was treated in an excess of standard $AgNO_3$, and 1 ml of indicator – a nitric acid solution of ferric sulfate – added at the same time. The red crystals were immediately destroyed, with the formation of silver iodide. The liquid and precipitate were left to stand until all the dark particles disappeared. To accelerate the reaction, the particles were broken up with a glass rod. After 20–40 minutes, twice its volume of water was added to the liquid and precipitate, and the excess silver back titrated with ammonium thiocyanate. The equivalence point was determined not only by the indicator, but also by the appearance of a grey color in the precipitate.

Bismuth was determined as the oxide. 0.2–0.3 g of the compound was treated with excess concentrated nitric acid and heated slightly. After removal of the iodine as vapor the weak nitric acid solution was diluted with water, and, after addition of ammonium carbonate, the bismuth in the precipitate was determined gravimetrically. Water was determined by taking 0.3 g of the air-dried material in a beaker and keeping it in a drying oven at a temperature of 150–155°. When drying was finished, the beaker was immediately closed with a ground glass stopper and cooled in a desiccator over P_2O_5. Under these conditions the dry chocolate-brown precipitate changed its color only very slightly, as a result of absorption of moisture during weighing. Benzidene was determined by difference.

The results are given in the table.

TABLE

	Found in, separate determinations		Average %	
Iodine	59.42	59.57	59.59	59.53
Bismuth	19.62	19.72	19.58	19.64
Water	3.49	3.47	3.51	3.49
Benzidene (by difference)		–	–	17.34

The analytical results lead to the following formula for the red crystals: $H_2N \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2 \cdot H_2[BiI_5] \cdot 2H_2O$.

Thus, the compound is a benzidene salt of pentaiodobismuthic acid with two molecules of water of crystallization.

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DETERMINATION OF MINIMAL QUANTITIES OF ARSENIC IN ORGANIC COMPOUNDS BY MEANS OF BIVALENT CHROMIUM SOLUTION

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Having considered the complexity and awakwardness of the methods recommended for the determination of arsenic in organic compounds [1,2] we decided to determine arsenic by means of a solution of bivalent chromium. The presence of antimony and other contaminants should not affect the accuracy of the determination.

As our experiments have shown, antimony ions are reduced by bivalent chromium in a neutral medium, while arsenic (V) is reduced in acid media. In acid media arsenic is reduced by bivalent chromium to metallic arsenic, which is filtered off and determined iodometrically. The reaction proceeds according to the following equations.

1. $As^{5+} + 5Cr^{2+} \longrightarrow As^{0} + 5Cr^{3+}$.

2. $2As^{\cdot} + 5I_2 + 8H_2O \rightleftarrows 2AsO_4^{3-} + 10I^{-} + 16H^{+}$

   $(NaHCO_3) \qquad HCO_3^{-} + HOH \rightleftarrows H_2CO_3 + OH^{-}$

$NaHCO_3$ is added to prevent reduction of arsenic acid to arsenous acid by the action of iodine ions.

The arsenic content is calculated from the following formula:

$$As = \frac{N_I(V_1 - V_2)\cdot 74.91}{1000\cdot 5} \text{ in grams,}$$

where V_1 is the total amount of iodine in ml; V_2 is the excess of iodine solution in ml; 74.91/5 is gram-equiv. of As.

For the determination of arsenic in urine, the latter is acidified with HCl (30% by vol) and an excess of bivalent chromium solution added in a stream of CO_2. Quinquevalent arsenic is reduced to the elemental state on heating to 100°.

The arsenic which separates out is filtered off, and washed with 5% NH_4Cl until a neutral reaction is obtained. The precipitate and filter paper (paper pulp can be used for rapid filtration instead of filter paper) are transferred to a flask fitted with a ground glass stopper, and 10-15 ml of a 2% solution of $NaHCO_3$ plus a known volume of standard iodine solution added. The excess iodine is back-titrated after 5-10 minute against sodium arsenite or sodium thiosulfate.

Results of determinations are given in Table 1.

TABLE

As taken, in g	As found, in g	As taken, in g	As found, in g
0.002	0.002	0.0006	0.0006
0.002	0.002	0.0006	0.0006
0.0068	0.0068	0.0006	0.0006
0.0036	0.0036	0.0006	0.0006
0.0036	0.0036	0.0006	0.0006
0.0068	0.0068	0.0006	0.0006

These results on the determination of arsenic introduced into urine as sodium arsenite show that arsenic (V) can be determined in amounts of 0.5 mg/liter In organic compounds (neosalvarsan) arsenic is determined as follows.

An aliquot of the organic compound (neosalvarsan) is decomposed with concentrated nitric acid (sp.gr.1.4) in the presence of 2% $KMnO_4$ (the decomposition is repeated). On cooling, a concentrated solution of sulfuric acid is added, and the solution heated till the appearance of white fumes. When this solution is cold, water is added and then HCl (30% by volume of the solution). An excess of a solution of bivalent chromium is added in a stream of CO_2 and the whole heated to 100°. The metallic arsenic is then treated as described above. Results are given in Table 2.

For the determination of arsenic in urine, the daily (24 hour) urine of a patient is concentrated to a volume of 100-200 ml, and is treated with HNO_3 (sp. gr.1.4) in the presence of 2% $KMnO_4$ (10 ml).

The solution is evaporated to a volume of 80 ml and subjected to oxidation until it stops frothing.

The nitrates are converted into sulfates. Arsenic is then determined in the light yellow, clear solution as described above.

TABLE 2

As taken, in g	As found, in g
0.0038	0.0037
0.0038	0.0037
0.0019	0.0019
0.0019	0.0019
0.0019	0.0018
0.0019	0.0020
0.0019	0.0018

Arsenic in amounts of 0.5 mg/liter can be determined.

This method of determining arsenic (in urine) which has been developed for clinical laboratories can also be used in forensic laboratories.

The Cr^{1+} solution used can be prepared by the author's electrolytic method [3,4] or by Popov's method [5].

SUMMARY

A rapid and accurate method has been developed for the determination of arsenic in organic compounds (in urine and neosalvarsan) based on the reduction of arsenic to the elemental stage by a solution of bivalent chromium.

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A METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF COPPER

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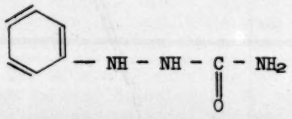
Phenylsemicarbazide, $C_6H_5-NH-NH-CO-NH_2$, reacts with copper salts to form yellow or red colors according to the amount of copper. The color obtained changes instantaneously to a golden yellow on the addition of an ammonia solution. The formation of this yellow color is a highly sensitive reaction and has been used by us for the colorimetric determination of copper as described below.

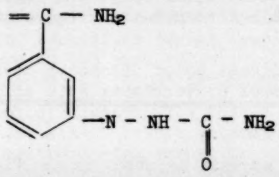
Colorimetric comparison is made by means of standard solutions with a constant relative difference between the concentrations of adjacent solutions in test tubes of thin colorless glass. The diameter of the test tube is 0.9 cm, the height of the solution in the test tube 7 cm and the volume 5 ml.

Characteristics of the New Method For The Colorimetric Determination of Copper

Phenylsemicarbazide is mentioned in the literature as a medicine under the patent name "cryogenin" [2], while in other literature sources the name "tryogenin" is applied to metabenzamidosemicarbazide [4,5]:



Phenylsemicarbazide



Metabenzamidosemicarbazide

An aqueous solution containing 0.1 g of phenylsemicarbazide in 100 ml water is used as the reagent [1].

We adopted the following order for carrying out the reaction: 0.6 ml of

---

1) Synthesis of phenylsemicarbazide: 28.8 g of phenylhydroazine hydrochloride and 18 g of urea are carefully mixed and ground in a porcelain mortar and the mixture placed in a round bottomed flask. It is then heated at 150-160° for 4-6 hours on an oil bath [6]. The melt after cooling is ground and worked up with 300-350 ml distilled water heated to the boil. The hot solution is immediately filtered. The precipitate which separates after cooling is sucked free of mother liquor, rapidly, and washed with cold water after which it is recrystallized twice from alcohol. The final product is dried in a vacuum desiccator over calcium chloride. The pure compound melts at 171°.

the reagent is added to ca. 4 ml of test solution and the volume made up to 5 ml. To increase the rate of the reaction the test tube may be immersed in boiling water. The contents of the test tube should be heated to 91-92°, after which they are cooled and a drop of 10% ammonia solution added. When this is done the weak yellow or rose color changes immediately into a golden yellow color.

The reaction is fairly specific. The majority of colorless cations do not interfere. The most suitable concentration range for the colorimetric determination of copper is 0.025-5 μg in 5 ml (Table 1).

TABLE 1

Conc of copper in μg/5ml; height of layer in test tube 7 cm.		Difference in conc. between adjacent solutions, in percent	Number of standards	Observations
From	To			
0.01		-	-	Gives a color which is already different from that of the blank.
0.01	0.015	30	2	
0.015	0.25	20	3	
0.025	5	10	55	
0.17	0.3	5	11	
5	8	20	4	
8	12	30	4	
	>12	No difference		

The curve for the absorption[1] of light is shown in Fig. 1

The high value for log ε (~5) in the region of maximum absorption confirms the high sensitivity of this reaction.

The yellow color obeys the Buger-Beer law for certain concentration ranges of copper (Fig. 2).

The highest color intensity develops when the neutral or very weak acid solution of copper is heated with reagent (before addition of ammonia).

Large amounts of other salts NH_4Cl, NH_4NO_3, $NaNO_3$, NaCl, Na_2SO_4 and K_2SO_4 lower the color intensity; their effect becomes perceptible when their ratio to copper becomes 10,000 mol/mol copper. Nitrates have a smaller effect than chlorides and sulfates.

During the determination of very small amounts of copper (of the order of a microgram and fractions of a microgram), we came up against losses of copper as a

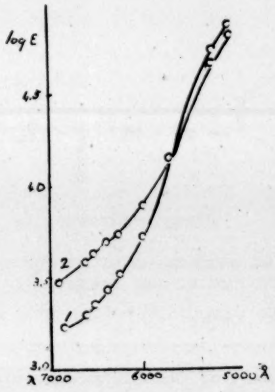


Fig. 1 Light absorption curve for copper solutions containing 0.2 μg of copper/ml; cell length 5 cm.
1) Measurements made immediately after heating, 2) measurements made after 24 hours.

1) A spectrophotometer of the Konig-Martens type was used. The apparatus was kindly lent by the Kharkov Sci. Research Institute of Metrology and Standardization.

result of adsorption on the surfaces of the flasks used. The following special experiments were accordingly carried out; a copper solution was placed in a porcelain basin and evaporated to dryness, the dry residue was worked up with 3 drops of nitric acid and again evaporated to dryness, then extracted 3 times with 1 ml lots of water; the extracts were all collected in one test tube; to this mixture 0.6 ml of reagent was added; the total volume was made up to 5 ml and the solution heated and ammonia added. These experiments showed that at low copper concentrations, the copper could be recovered practically completely after such a treatment. But on increasing the amount of copper the relative amounts of copper recovered decreased (Table 2).

By extracting the copper with hot water, followed by prolonged heating, low results were obtained (Table 2), possibly as a result of hydrolysis of copper salts.

A threefold extraction with cold water, in which the water was allowed to stay in contact with the dry residue for 10 minutes after addition of each lot, gave satisfactory results at low concentration and improved the results at high concentrations. Increasing the duration of the water treatment to 20 minutes

TABLE 2

Copper taken in μg	Copper found in μg					
	Nitrate	Sulfate	Acetate	Extraction with prolonged heating	Extraction with cold water on standing	
					10 min	20 min
0.12	0.10	0.10	0.12	0.05	0.12	0.14
0.24	0.13	0.18	0.19	0.06	0.24	0.27
0.48	0.25	0.24	0.37	0.09	0.37	0.50
0.96	–	–	–	–	0.67	0.99

made it possible to determine large amounts of copper satisfactorily (Table 2). New, unused porcelain basins even under the best conditions do not completely give up their copper. After repeated determinations in the same basins their surfaces become gradually saturated with copper, the amounts of copper determined increase and finally approach the normal values (Table 3, Columns 1,2).

The method of cleaning the surfaces of the beakers before determining the copper is very important. By very vigorous treatment, e.g., immersion in nitric acid (1:4) and boiling, the surfaces are completely freed from copper and start to adsorb copper again when they are used for subsequent determinations, until the surface becomes saturated (Table 3, Columns 3,4,5).

It was found that constant results could be obtained by the following method of cleaning; 1-2 ml of concentrated nitric acid is placed in the basin and heated on the water bath (2-3 minutes until fumes appear), the acid at this stage is not at a temperature greater than 60°, the acid is poured off and the beaker rinsed several times with water. This operation is repeated three times.

The results of experiments which characterize the losses of copper as the result of adsorption are given in Table 3.

Gurevich [8] observed a similar behavior for the adsorption of lead by the surfaces of flasks.

In 1933 Sarata proposed a colorimetric method for the determination of copper by means of metabenzamidosemicarbazide in the presence of lead acetate [3,4]. On heating, the copper solution with this mixture for 40-50 minutes at 40°, a red color develops which can be used for colorimetric determination.

According to Sarata, 0.5 to 30 μg of copper can be determined by this method.

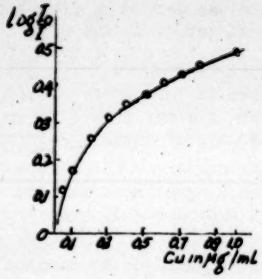


Fig. 2 Curve for the optical density of copper solutions of different concentrations. Determinations were made at a wave length of 4960 A; cell length 1 cm.

In so far as phenylsemicarbazide also gives a similar reaction with copper salts, we investigated the conditions for the colorimetric determination of copper by means of the red color; the latter appears under the conditions given above in the absence of lead acetate as well, but it is not so intense. The intensity and shade of the red color is strongly dependent on the ratio between the amount of copper and reagent. The greatest intensity for the red color is observed for a ratio of 1 mol copper to 12 mols of reagent. With increasing concentration of lead acetate the color intensity increases up to a ratio of 1 mol copper to 10 mols lead acetate. Further increase in the amount of lead decreases the intensity.

The curves for the absorption of light in copper solutions containing 0.2 μg/ml for a constant ratio between the amount of copper and phenylsemicarbazide (1 mol copper to 12 mols reagent) and for different amounts of lead acetate are given in Fig. 3.

TABLE 3

Copper taken in μg	Copper determined in μg				
	New basins		Old basins, cleaned by boiling in nitric acid		
	1	2	3	4	5
0.12	0.10	0.10	0.10	0.10	0.11
0.24	0.13	0.18	0.13	0.16	0.22
0.48	0.18	0.40	0.21	0.36	0.44
0.96	0.54	0.78	0.52	0.74	–

The value of log ε in the region of maximum absorption indicates the lower sensitivity of the given reaction in comparison with the reaction which we have proposed. This is confirmed by the results on the concentration limits of copper which are most suitable for colorimetric determination according to the red color (Table 4).

The necessity of observing a definite ratio between the amount of copper and the reagent in order to get comparable colors requires a knowledge of the approximate content of copper in the test sample. This is a big drawback and limits the practical application of the method.

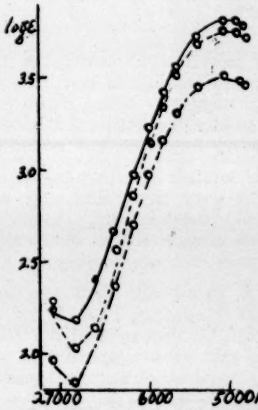


Fig. 3 Light absorption curves for different concentrations of lead acetate: 1) 1 mol; 2) 10 mols and 3) 14 mols.

The method which we have proposed involving the use of phenylsemicarbazide, and based on the formation of the golden-yellow color after heating and addition of ammonia, is free of these drawbacks and is twenty times more sensitive than Sarata's method [4].

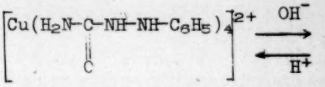
In order to elucidate the nature of the colored product formed, solutions of the product were electrolyzed.

During electrolysis of the red solutions obtained by heating a solution of a copper salt with phenylsemicarbazide in the course of 40 minutes to 40°, a transfer of the red color to the cathode immersed in agar-agar is observed. A similar transfer of the red color to the agar-agar during the time of experiment was not observed in a control test. On repeating the experiment with the yellow solution, penetration of the yellow color into the agar-agar layer was observed in the case when the electrode immersed in the agar-agar was made the anode. Consequently, the red color of the solution is determined by the presence of red cations, and the yellow color by yellow anions. The composition of the yellow complex was investigated spectrophotometrically by Job's method [7]. As a result the curve depicted in Fig. 4 was obtained.

TABLE 4

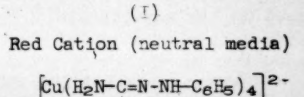
Concentration of copper in μg/5ml (height of layer 7 cm)	Difference in concentration between adjacent solutions percent	Number of standards	Observations
1	-	-	Gives a color already distinguishable from blank
From 1 to 2	20	4	
2 to 22	10	23	
22 and higher	>10	-	

On the basis of what has been said we suggest that the structure of the red and colored compounds is analogous to the ammine complex of copper



(I)

Red Cation (neutral media)



(II)

Yellow anion (alkaline media)

The copper in these complexes can hold the phenylsemicarbazide by means of the (free) pairs of electrons of the NH_2 group. It is well known that these groups determine the basic properties of phenylsemicarbazide.

Doubly charged cations with a red color(I) can be formed in a neutral medium. In an alkaline medium the stability of complex (I) is apparently maintained, but favorable conditions are created for the enolization of four carbonyl groups. As a result a doubly charged anion with a yellow color is formed with the probable structure (II).

Determination of copper in blood

Blood was chosen for testing the method developed, first because it is one of the difficult objects in analysis and secondly because the development of a method capable of wide application for the determination of copper in blood would be very useful for clinical purposes.

Even the most sensitive of known methods requires no less than 0.5-1 ml of blood. The sensitivity of our method makes it possible to decrease this volume to 0.1 ml; this is of considerable significance.

According to results in the literature, the normal content of copper in human blood amounts to 120-150 μg/100 ml. The amount of iron is more than 400 times as much.

It was demonstrated that for concentrations of iron less than 0.4 μg/5ml no color is formed with phenylsemicarbazide. For amounts of 0.5 μg and over, a pale yellow color develops which is not proportional to the iron concentration.

The following experiment showed that iron could be separated by means of hydrolysis.

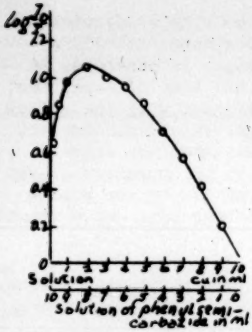


Fig. 4. Light absorption curve by Job's method. 0.001 M solutions of copper and phenylsemicarbazide were used in the experiments.

A solution containing 50 μg iron (0.1 ml of blood contains this amount of iron) was evaporated to dryness in a porcelain dish. The dry residue was treated with 3 drops of concentrated nitric acid and evaporated on a water bath, worked up with 3 drops of water, and evaporated again. The dry residue was worked up 3 times with water, (1 ml of water each time), and the volume finally made up to 5 ml. On addition of phenylsemicarbazide to the solution thus obtained, the liquid remained colorless. It is clear therefore that iron remains practically insoluble under these conditions. By separating 0.12 μg of copper and 50 μg iron in this way and subsequently determining the copper in the aqueous solution, satisfactory results were obtained (Table 5).

For the determination of copper in 0.1 ml of blood taken from the same person's finger by pricking with a needle, the residue after ignition of the blood in a muffle was worked up with nitric acid and water as described above. When this was done the copper content found in separate determinations was 0.10, 0.18, 0.10, 0.12, 0.15, 0.15, 0.15, 0.15, 0.15 μg of copper.

These values for the copper content of blood are in good agreement with results in the literature.

Results for the determination of copper in blood with and without the additon of a known weight of copper are given in Table 6. 0.1 ml of blood was taken for testing.

TABLE 5

Iron taken, in μg/5ml	Copper taken, in μg/5ml	Copper found, in μg	Iron taken, in μg/5ml	Copper taken, in μg/5ml	Copper found in, in μg
50	–	Colorless Solutions	–	0.12	0.10
50	–	"	50	0.12	0.15
50	–	"	50	0.12	0.10
–	0.12	0.12	50	0.12	0.10
–	0.12	0.12	50	0.12	0.10
–	0.12	0.14			

TABLE 6

Copper added, in μg	Amount of copper that should be present, in μg	Copper found, in μg	Deviation, in μg	Recovery, percent
–	–	0.12	–	–
–	–	0.12		
0.12	0.24	0.24	0	100
0.12	0.24	0.25	+0.01	105
0.24	0.36	0.34	−0.02	94
0.48	0.60	0.55	−0.05	92
0.48	0.60	0.67	+0.07	112
0.48	0.60	0.55	−0.05	92

The results in Table 6 show that it is possible to determine copper in blood by the method proposed with an error of not more than 10%.

Instructions for the Determination of Copper in Blood Reagents

a) 0.1 g of phenylsemicarbazide in 100 ml serves as the reagent. The solution

is prepared in small amounts daily since the solution starts to turn yellow 2-3 days after preparation.

b) Water. For this work water twice distilled from glass vessels is used. "Pyrex" flasks cannot be used, since it was observed that water from such flasks decreases the sensitivity of the reaction. In doubtful cases blank tests should be carried out on the water.

c) Concentrated nitric acid. If a blank test gives colored solutions then the acid should be purified by distillation.

d) 10% Ammonia solution. If a blank gives a color, then the aqueous ammonia solution should be prepared by distillation of ammonia into twice distilled water with cooling.

Apparatus. a) For ignition of blood samples porcelain dishes with unscarred enamel and not more than 5 cm in diameter should be used.

It is difficult to achieve complete ignition of organic compounds in dishes with rough surfaces. Pyrex dishes and ones of transparent quartz did not give satisfactory results in our experiments.

The dishes to be used should be tested beforehand. Standard solutions of copper should be used, the concentrations of which are similar to those of the test solutions, in order to ascertain whether or not copper is adsorbed by the dish surfaces. If the amount of the copper found is less than that taken, then it is necessary to evaporate solutions of copper of similar concentrations to the test solutions from the dishes several times.

b) Cleaning of the dishes after analysis. Most of the dry residue is removed with moist lumps of some soft material. After this treatment the dish is worked up three times with concentrated nitric acid, the contents being heated on the water bath for 2-3 minutes. After each nitric acid treatment the dish is washed with water. Dishes used for copper analysis should not be used for any other purpose.

c) The test tubes in which the colors are compared should be made of thin, colorless glass, without seams, and should have a diameter of ca. 10 mm; 5 ml of liquid should fill them to a height of not less than 7 cm. The test tubes should be stored full of distilled water. When necessary the surfaces should be cleaned by washing with nitric acid.

Preparation of Standard Solutions

500 mg of electrolytic copper is dissolved in 5 ml nitric acid, 1:1, and the solution thus prepared made up to 500 ml. Such a solution contains 1 mg/ml. Two other solutions are prepared from this primary standard, one containing 1 μg/ml and the other 0.1 μg/ml. These can be used for preparing a series of standards.

A 2 ml pipette with scale divisions of 0.01 ml is used for measuring out the standards. 5 standards (less and greater than 0.12 μg) are sufficient: 0.084, 0.12, 0.17, 0.24 and 0.34 μg copper in 5 ml.

The difference in concentration between two adjacent solutions in this series is 30%. Interpolation between these standards enables determinations to be made with an accuracy of up to 10%.

1. Blood Sampling. Test samples are taken from a finger by pricking with a needle. The blood is collected in a micropipette of 0.1 ml capacity one drop of blood should be enough for duplicates. The blood is transferred from the pipette to a dish containing 3 drops of concentrated nitric acid. The blood is immediately carefully mixed with nitric acid by a rotary motion of the dish until a uniform mixture is obtained.

2. Ignition. The contents of the dish are dried on a water bath, after which it is placed in a muffle at a dark-red heat. Complete ignition usually takes 15-20 minutes. After ignition there remains a dark, grainy residue which becomes red on cooling. A gas burner cannot be used for this ignition.

3. Extraction of copper and colorimetric determination. The residue from ignition is treated with three drops of concentrated nitric acid, dried on a water bath, then treated with three drops of water and again dried. The dish is removed from the bath, treated with 1 ml of water, and allowed to stand for 20 minutes, the dish being periodically shaken with a rotary motion. The water extraction is repeated 3 times.

To the solution poured into a test tube 0.6 ml of the phenylsemicarbazide solution is added and the volume made up to 5 ml.

The test tubes containing the test solutions and those containing the standards are immersed simultaneously in water, and heated until the contents have a temperature of 92°.

After cooling, one drop of 10% ammonia solution is added to each test tube and the contents mixed with a thin glass rod. The colors are then compared. It is possible to carry out a series of analyses simultaneously.

The present research was done under the direction of Prof. V.G.Gurevich.

SUMMARY

A new, very sensitive colorimetric method is proposed for the determination of copper. Amounts of copper as low as 0.025 μg/ml can be determined with a relative error of not more than 10%.

The method does not require the use of organic solvents.

As an illustration of its application in practice, the determination of copper in blood may be quoted. 0.1 μg of copper in 0.1 ml of blood can be determined. A method has been worked out for the separation of copper from iron.

It has been shown experimentally that the colorimetric determination of copper by means of phenylsemicarbazide in the presence of lead acetate by means of the red color developed is not very suitable as a practical method.

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Received December 14, 1949

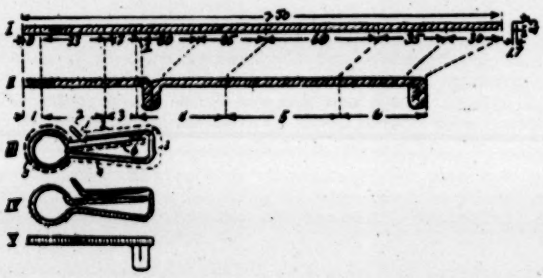
A NEW CLIP

D.M.Borinets

Clips of the Mor type are used in all chemical laboratories. This clip has certain disadvantages.

It constricts the tube on one side more than on the other. It is impossible to regulate the constrictive force of the clip according to the elasticity of the tube. It is difficult to restore the lost constrictive force of the clip. In order to fit the clip on to a tube, one end of the tube has to be free.

The new type of clip which I have designed is free from all these disadvantages of the Mor type. The method used for making one of these clips is very simple (see diagrams). Iron 3 mm wide is flattened out to give a wire of the dimensions 3.5 X 1.7 mm (I). It is then bent into shape (II) and then into (III) as shown in the diagrams. The dimensions indicated are optional. According to what tubes the clips are to be used on, the cross sections and the length of the wire may be varied. It is advisable to anneal those points on the wire where it is to be bent, before the actual bending.



Working drawings for making a clamp as constructed by Engineer D.M.Borinets.

I – 3 mm steel wire, flattened to 3.5 X 1.7 mm;
II – Same wire with grips bent;
III – Finished clamp (bending scheme), top view;
IV – Clamp in use;
V – Lateral view of clamp.

Received February 4, 1952

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CHRONICLE

THE CONFERENCE ON ANALYTICAL CHEMISTRY IN GORKY

A regional conference on analytical chemistry was held from the 4th to the 6th of June in Gorky. About 260 people participated, including scientific workers from Moscow, Leningrad, Kiev, Saratov and many other towns, and also workers from the chemical industry in Gorky itself. The work of the conference which proceeded apace, apart from plenary sessions, was divided up among different sections.

Altogether 40 papers were heard

A number of reports was devoted to the theory of the action and application of organic reagents in analysis.

In V.I.Kuznetsov and L.M.Kulberg's report the effect of the structural characteristics of the molecules of an organic reagent on its reactivity was considered. In depicting the so-called characteristic atomic group, this influence was not taken into account, and consequently the presence in the molecules of different reagents of "one and the same" grouping does not always indicate similar reactions for these reagents.

I.S.Mustafin showed that a similar simplified conception exists regarding the effect of the molecular weight of a reagent on the solubility of the reaction products. Only in homologous and similar series of reagents does the solubility decrease regularly with increasing molecular weight of the reagent, the weighting effect".

The completeness of the precipitation of tungsten by organic reagents is determined by the nature of the precipitant and the state of the tungsten in solution (normal tungstates, para, meta). The most complete precipitation of all forms of tungsten is effected by salts which are not too weak basically and have a high molecular weight—alkaloids, methylene blue, methyl blue, methyl violet, rivanol, etc. (B.A.Platunov).

V.I.Kuznetsov compared colorimetric determinations with one and two colored reagents. The latter necessitate working at very precise pH values and are less selective; reagents of this type however are known for almost all the elements, and the reactions are more sensitive.

In the colorimetric determination of nickel in the presence of cobalt and other elements it is convenient to extract the nickel dioxime complexes, which in the case of difuryl- or diphenyl-dioxime are more intensely colored than the dimethylglyoxime (V.M.Peshkova). Methyl violet which gives colored solid phase reactions is used for the determination of microgram quantities of tungsten and mercury. Mercury is determined in the presence of bromides of iodides (A.F. Nemirovskaya, M.P.Ananevskaya) Mercurized analine and other amines are suitable for the microcrystalloscopic detection of a number of anions (A.A.Belyakov).

V.F.Barkovsky and L.M.Kulberg read a paper on the colorimetric determination of platinum by means of a blue color formed by chloroplatinates with acetamide. For the determination of traces of Cl, L.D.Borzova and L.M.Kulberg used the formation of intensely colored indophenols. For the colorimetric determination of boron a new reaction involving the use of azomethane dyes from H-acid and salicylaldehyde is applied (T.I.Badeeva and L.M.Kulberg).

K.B.Yatsimirsky in his report indicated the expediency of the thermodynamic approach to the solution of various problems in analytical chemistry. A.K.Babko reported on the application of silico- and phospho-molybdic acids in analysis and the study of their compounds by the Ostromyslensky–Job method and the limitations of this method.

In the section on the polarographic and chromatographic methods reports were read by V.B.Avilov on the physico-chemical bases of the iodometric determination of As, Sb, Fe, Sn, Cr, V, and the theoretical basis of certain oxidation-reduction methods. V.F.Toropova read a report on the results of the polarogaraphic investigation of the acetate complexes of Pb and Cu which confirmed the effects of acetate buffers which have been previously observed.

A.M.Vasilev, V.F.Toropova and A.A.Busygina reported on the possibility of separating Cu, Cd, and Zn by ion exchange on Wofatit P, using solutions containing thiosulfate and acetate. V.N.Lenskaya and L.M.Kulberg studied selective reduction on ion exchange compounds. It seems that in the case of MnO_4^-, $Cr_2O_7^{2-}$ and CrO_4^{2-} ions selective reduction is observed which varies according to the experimental conditions and the nature of the ion-exchange resin.

V.P.Millin discussed the experimental and theoretical bases of electrography. M.L.Tsap reported on the photoelectric absorptiometer FA-52 which is simply constructed and can be used for the wave length range 400-1300 mμ and on the potential uses of the near infra-red for analysis.

Interesting papers were read on topochemical reactions (L.M.Kulberg) and on F.I.Flavitsky's reaction, which occurs during the pulverization of solid materials. (I.M.Isakov) (e.g., for the determination of the higher valency states of the rare-earth elements). The development of Flavitsky's reaction led to new rapid methods for diagnosing and decomposing minerals. Yu.G.Titova reported on micromethods for the determination of selenium.

Papers on sanitary-hygiene analysis were heard at the conference: the determination of tetraethyl lead in air by absorption with an alcoholic iodine solution (E.V.Gernet); the determination of silico-organic compounds in quartz in the presence of silicates, using the unequal relation of these compounds to H_6SiF_2 (S.S. Gurvits); the determination of a number of aromatic amines and phenols, by conversion into colored and fluorescent compounds (D.N.Vaskevich) et al.

The analysis of organic compounds was discussed; rapid micro-methods for the simultaneous determination of several elements (M.O.Korshum, V.A.Klimova, N.S. Sheveleva, E.G.Bereznitskaya) et al.

A number of reviews were heard at the conference; on the polarographic determination of organic compounds (I.A.Korshunov); the determination of organic sulfur compounds in gases used for catalytic synthesis (S.N.Kazarnovskyy) et al.

V.I.Kuznetsov

CRITICISM AND BIBLIOGRAPHY

"Scientific Reports of Kharkov State University", Vol. 37.

"Proceedings of the Scientific-Research Institute of Chemistry", 1951, Kharkov, 170 pp. Circulation 500.

"The Collection of the Proceedings of the Scientific-Research Institute of Chemistry" contains 24 articles on different questions in analytical chemistry. N.P.Komar is either the author or one of the participants in 17 of these papers; altogether 17 chemists participated in the work reported.

The volume of the proceedings under review is not devoted to one theme, though 18 of the articles relate to various problems in colorimetric analysis, spectrophotometry, and the chemistry of colored compounds. The wide application of mathematical methods for the characterization of various equilibriums and processes of importance in analytical chemistry is a feature which is common to all the articles. Five of N.P.Komar's papers devoted to a number of fundamental problems in the colorimetric method of investigating multicomponent systems are of the greatest importance. The study of the composition and properties of colored compounds in solutions has been taken up by a number of investigators recently.

The method of physico-chemical analysis of solutions enables a number of questions which are of importance in colorimetry and in the chemistry of colored compounds to be solved. The method of equimolecular mixtures suggested by Ostromyslensky[illegible] and developed by Job and other investigators is of great interest for the determination of the composition of complexes in solution. In the first of Komar's articles mentioned above it is shown in a general form, that by means of this method it is not the composition of the colored complex that is determined, but only the ratio between the coefficients of the reaction equation. Therefore in a case where one of the components participates in a side reaction, complications arise which must be taken into account.

In other articles a number of questions on the methods of determining composition, dissociation constants, and the optical characteristics are considered for the case of the formation of two colored compounds, and further in cases where the color of the reagent depends on the pH of the solution, etc.. Two articles by V.N.Tolmacheva are devoted to similar questions. In these papers a number of formulae is given which considerably facilitate the calculation of the basic characteristics of a system on the basis of the observations made.

A number of articles by the same authors and also by L.P.Adamovich and others are devoted to investigations of individual colored compounds; the quinalizarin-beryllium complex; the compounds of zinc with methylviolet and thiocyanogen, and reactions for cadmium and cobalt. All these articles are also distinguished by detailed mathematical treatment of the questions and give a series of new and important characteristics for individual reactions. The composition of the majority of the colored compounds investigated are determined as well as their optical constants and the instability constants or their equilibrium formation. The experimental part of these and other papers indicate a sound approach on this side of the investigation.

In some of the articles calculations and experimental results are given for

various questions in chemical analysis, e.g. the method of determining nitrites in the presence of nitrates, and the chromate method for the determination of sulfates, etc.. Finally, there are four articles which are included under the general heading of 'The mathematical evaluation of the sensitivity of chemical reactions". In these articles on the basis of the work of a number of investigators and by the adoption of a mathematical treatment of the results, the range for positive reactions for sulfates, iron and ammonium ions and also the effect of certain reaction conditions are evaluated.

This short review given above of the contents of the Collection shows it to be of great interest. Almost all the articles are original scientific researches. Every chemist who is interested in the question of physico-chemical analysis of solutions and also in some of the individual reactions mentioned above will find valuable material in the Collection. On the other hand the high scientific level of the work enables one to forecast a large demand for the Collection. In this connection therefore it is essential to point out a number of deficiencies.

The articles of N.P.Komar and V.I.Tolmacheva mentioned above on the optical method of investigating equilibria unfortunately give only algebraic interpretations; the geometrical method is hardly used although it is more graphic. In addition the formulas deduced are usually not written down in a "workable" form. There are no lists of symbols and sometimes, (e.g., on p. 74, etc.) there are symbols the meanings of which have to be sought for in other articles. This hinders the introduction of these formulas into practical experimentation.

The authors are often carried away by the form of the mathematical calculations. As a result the methods master the authors when it should be otherwise. In some cases detailed calculations are made in connection with certain aspects of a process which are not the basis of the method. Thus, N.P.Komar's experimental results on a method for eliminating adsorption in the chromate method of determining sulfates are undoubtedly interesting, nevertheless the results have not direct bearing on the calculation of the solubility of barium chromate in trichloroacetic acid. Meanwhile, in order to carry out the calculations actually made, a complex procedure is adopted, including extraction of activity coefficients, equations of the 5th order, and solutions involving three successive approximations. While as the result of the author's excessive faith in Landolt's tabulated results, calculations yielding results which differ by as much as three times from N.P.Komar's experimental results are made.

Sometimes the effect of non-aqueous solvents on dissociation is not taken sufficiently into account and the physical mechanisms of certain processes are not always considered correctly. Thus, L.P.Adamovich in his article on the quinalizarin-beryllium complex calculates the instability complex; in order to do this the total concentration of beryllium uncombined in the colored complex is taken as the concentration of the free beryllium ions. In a medium of 0.3 N alkali, however, the beryllium ion cannot exist in a free state. The indicator properties of quinalizarin are also not explained. Thus, in effect, it is the equilibrium constant of the reaction which is calculated and not the instability constant of the complex. This does not detract from the value of the results obtained, nevertheless the determination applies to another equilibrium.

In the study of systems involving solid phase reaction products several important factors were not taken into account. In the physico-chemical analysis of solutions, maxima and other characteristic points are observed on the property-composition diagram. Nevertheless these special points serve as a basis for making conclusions as to the composition of a compound only when there is a proportionality between the numerical values of the property considered and the concentration of the respective compound. At the same time the absorption of light by suspensions of a colored insoluble compound may depend not only on the amount of solid in unit volume of suspension, but also on the particle size of the solid. L.P.Adamovich and P.V.Starchenko in their article on the reaction between zinc and methylviolet observed this phenomenon but do not adduce any results on testing the effect. It is possible that this fact (or others) may be the reason for the rather improbable

conclusions which the authors reach, viz., that methylviolet, zinc and the thiocyanate ion are found in the ratios 6:1:4 in the complex; on this assumption it follows that a cation with four charges should be precipitated and not a neutral molecule (see equation p. 28).

It is not sufficient to use chromatographic methods for checking the purity of organic reagents. Some preparations, e.g. quinalizarin, are rarely individual compounds.

There are some editorial errors and inappropriate expressions on p. 10 "adsorption" is used for absorption; on p. 15 there is an expression "Results in an exaggerated form" p. 17 " complex forming compounds are decanted"; p.23 "changing competitors," etc.

Despite these drawbacks the Collection contains very valuable material. In the articles included new and important steps are made in the development of the optical method of investigating solutions and a number of other questions in analytical chemistry. The Collection characterizes the high scientific level of Soviet analytical chemistry and the undoubted sucess of the Scientific Chemistry and the undoubted success of the Scientific Collection of the Institute.

A.K.Babko

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The Use of the Ultraviolet in Analytical Chemistry.
2. Quantitative Microchemical Analysis in the Ultraviolet. p. 221.

Fig. 1. Absorption spectrum and microphotograph of $PbCl_2$ and $PbBr_2$.

The Use of Diantipyrylphenylmethane in Analytical Chemistry. 2. p. 249.

Fig. 1. Crystal form of $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3 \cdot H_3[Fe(CN)_6] \cdot 9H_2O$. Magnification 80.

Fig. 2. Crystal form of $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2W_2Cr_2O_7$. Magnification 80.

The Reaction Between the Bismuth Ion and Benzidene. p. 269.

Fig. 1. Benzidene, $H_2[BiI_5] \cdot 2H_2O$. Crystallized from hot solution.

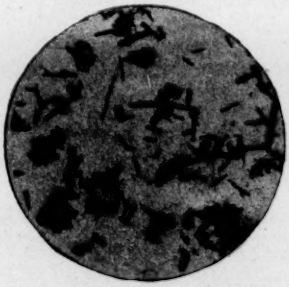

Fig. 2. Benzidene, $H_2[BiI_5] \cdot 2H_2O$. Crystallized from cold solution.

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A CRYOSCOPIC METHOD FOR THE DETERMINATION OF ARENES (AROMATIC HYDROCARBONS) IN LIGROIN, KEROSENE, AND GAS OIL PETROLEUM FRACTIONS OF STRAIGHT DISTILLATION

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A cryoscopic method which we have developed for the quantitative group determination of aromatic hydrocarbons is described in the present article. The method is based on the well known chemical thermodynamical principle that for dilute solutions, the depression of the initial crystallization temperature of a solvent is proportional to the amount of solute dissolved in it. This relation [1] can be expressed by the equation (1):

$$\Delta t = \frac{N}{A} \alpha N, \qquad (1)$$

where Δt is the depression of the initial temperature of crystallization ($t_{cryst.}$) caused by the solute; N is the percent molar concentration of the solute; A – the cryoscopic constant (the content of solute in mol. percent which gives rise to a depression of 1 deg in t_{cryst} of the solvent) which is characteristic for any given solvent; α is the depression of t_{cryst}, caused by 1 mol. percent of the solute.

It follows from equation (1) that for any given solvent the depression of its initial temperature of crystallization is proportional only to the content of the solute expressed in mol. percent, and is independent of the nature of the solute. This propoerty is used in the cryoscopic method proposed for the quantitative determination of aromatic hydrocarbons in petroleum fractions. The method is essentially as follows.

Cyclohexane is chosen as the solvent and its initial temperature of crystallization is determined. To the cyclohexane a small amount (ca.3%) of the petroleum fraction to be tested is added. The initial crystallization temperature of the cyclohexane is thereby lowered by a certain amount which is denoted by Δt_1 (e.g. 7.26°). The solution of the petroleum fraction in cyclohexane is then treated with concentrated H_2SO_4 under conditions described below. As a result of this treatment the aromatic hydrocarbons contained in the fraction originally added to the cyclohexane are removed and the total amount of the petroleum fraction contained in the cyclohexane decreases accordingly. The initial crystallization of the cyclohexane solution of the fraction will increase slightly. Let this increase be denoted Δt_2 (e.g. 1.46°):

$$\begin{array}{l} 7.26^\circ \ (\Delta t_1) \ 100\%, \\ 1.46^\circ \ (\Delta t_2) \ x\%. \end{array}$$

From which we find that

$$x = \frac{1.46 \cdot 100}{7.26} = 20.1\%, \text{ (molar)}.$$

or the fraction treated contains 20.1% (mol.) of aromatic hydrocarbons. The general form of the equation for calculating the aromatic hydrocarbon content in a test mixture on the basis of the experimental results is as follows:

$$x_{mol} = \frac{100 \cdot \Delta t_2}{\Delta t_1} \qquad (2)$$

where x_{mol} is the content of aromatic hydrocarbons in mol %; Δt_1 the depression of t_{cryst} for cyclohexane after addition of the test mixture; Δt_2 the elevation of the crystallization temperature of the solution of the test mixture in cyclohexane after the H_2SO_4 treatment.

From the example given above it is clear that for the quantitative determination of aromatic hydrocarbons by means of the cryoscopic method in the form described above, it is not necessary to weigh the cyclohexane or the fraction to be tested accurately. It is accurate enough to use a buret or pipet for adding ca.3% of the fraction or 0.3-0.5 ml according to the molecular weight. Not even a knowledge of the cryoscopic constant of the solvent is necessary.

In principle, any other individual solvent (i.e., not a mixture of solvents) can be used instead of cyclohexane as long as it does not react with H_2SO_4 and is a good solvent for petroleum fractions. Cyclohexane however has the following advantages: 1) a high value for α (1 mol % of a solute depresses the initial crystallization temperature of cyclohexane 2.42°); 2) the suitability of the value of the initial crystallization temperature (+6.55° for pure cyclohexane); and 3) it is comparatively easily available.

EXPERIMENTAL

Characterization of the Original Compounds and General Experimental Procedure

The original alkanes and cyclanes were given a preliminary treatment with 98% H_2SO_4 until there was no further change in their physical constants; they were then distilled. The original aromatic hydrocarbons did not contain more than 1.3% of alkanes or cyclanes. Petroleum fractions boiling in the ranges 150-200°, 200-250°, 250-300°, 300-350° and 350-400° were also used after removal of the aromatic hydrocarbons by adsorption on silica gel. That all the aromatic hydrocarbons had been completely removed was checked by passing the fractions repeatedly through a column packed with fresh lots of silica gel and testing their physical constants. Only in two cases (the 150-200° fraction from heavy Balakhany petroleum and the 300-350° fraction from Kalinsky petroleum) were the aromatic hydrocarbons separated by treatment with 98% H_2SO_4. All the fractions were obtained from individual petroleums. The petroleum aromatic hydrocarbons were isolated from individual petroleums by silical gel adsorption and were kindly placed at our disposal by our colleague M. S. Borova of our Institute. The properties of the original compounds are given in Table 1.

The temperature of crystallization was determined in a Beckmann apparatus used for molecular weight determinations, provided with an automatic stirrer. The temperature was measured by means of an ordinary thermometer graduated from -30 to +20° with scale divisions of 0.1°. The temperature could be read to an accuracy of 0.02° by using a magnifying glass. Since in this particular case it is a difference between points on the thermometer that has to be measured and not the absolute value of the temperature, an accuracy of the above order is sufficient. The cooling liquid used was alcohol plus solid carbon dioxide. The difference between the temperature of crystallization of any test mixture and that of the cooling bath did not exceed 1-2°.

10-13 ml of pure cyclohexane was introduced into the inner tube of the Beckmann apparatus and its initial temperature of crystallization determined. 0.3-0.5

TABLE 1

Physico-Chemical Constants of the Original Hydrocarbons and Fractions

No.	Designation of the hydrocarbons and fractions	Mol. wt	Crystallization temp., °C	B.p. ranges at 760 mm Hg	d_4^{20}	n_D^{20}	Critical solution temp. in aniline, in °C
1	Cyclohexane	84.2[3]	+6.00	80.45-80.65	0.7787	1.4260	-
2	Diethylbenzene (mixture of isomers)	134.2[3]	-	178.2-183.9	0.8637	1.4912	-
3	Decahydronaphthalene (mixture of isomers)	138.2[3]	-	-	0.8710	1.4690	+36.9
4	Pentamethylbenzene	148.2[3]	+57.3	-	-	-	-
5	1-Methylnaphthalene	142.2[3]	-	239.0-241.0	-	1.6090	-
6	Triethylbenzene (mixture of isomers)	162.3[3]	-	216.0-218.4	0.8813	1.4989	-
7	2,6-Dimethylnaphthalene	156.2[3]	+110-110.5	216	-	-	-
8	2-Phenylheptane[1]	176.3[3]	-	230.1-230.8	-	1.4892	-
9	1,2-Diphenylpentane	182.3[3]	+50.7	-	-	-	-
10	n-Hexadecane	226.4[3]	+17.2	-	-	1.4345	+68.8
11	Diamylnaphthalene (mixture of isomers)	268.4[3]	-	-	-	1.5520	-
12	Dicyclohexylindane (mixture of isomers) $C_{21}H_{30}$[2]	282.4[3]	-	178-179 (3 mm)	1.0011	1.5510	-
13	Alkane-cyclane part of the 150-200° fraction from Bibieibatsky petroleum	136.0[4]	-	150-200	-	1.4337	+60.9
14	Alkane-cyclane part of the 150-200° fraction from Balakhany heavy petroleum	141.0[4]	-	150-200	-	-	+60.5
15	Alkane-cyclane part of the 200-250° fraction from Kalinsky Petroleum	175.0[4]	-	200-250	-	1.4520	+67.5
16	Alkane-cyclane part of the 250-300° fraction from Kalinsky Petroleum	226.0[4]	-	250-300	-	1.4600	-
17	Aromatic hydrocarbon fraction 300-350° from Buzovinsk Petroleum	233.2[4]	-	300-350	-	-	-
18	Aromatic hydrocarbon fraction 350-400° from Buzovinsk Petroleum	258.8[4]	-	350-400	-	-	-
19	Alkane-cyclane part of the 300-350° fraction from Kalinsky Petroleum	263.0[4]	-	300-350	0.8479	1.4642	+89.2
20	Alkane-cyclane part of the 350-400° fraction from Buzovinsk Petroleum	293.0[4]	-	350-400	-	-	-

1) Was synthesized by I. L. Kotlyarevsky. 2) The sample of dicyclohexylindane was kindly placed at our disposal by E. S. Pokrovska. 3) The molecular weight was calculated on the basis of an empirical formula. 4) The molecular weight was determined experimentally by a cryoscopic method using benzene.

ml of the test fraction was then added to the cyclohexane and the temperature of crystallization of the solution determined. The solution was then treated with 1 volume of concentrated H_2SO_4 in order to remove the aromatic hydrocarbons, subsequently separated from the H_2SO_4 and washed successively with 10% NaOH and H_2O till the solution was neutral. The solution was finally dried over anhydrous $CaCl_2$. The crystallization temperature for this treated solution was finally determined.

The value of α, i.e., the depression of the crystallization temperature of cyclohexane as a result of the addition of 1 mol % of different hydrocarbons was determined by measuring the crystallization temperature of cyclohexane by the method described above before and after addition of the solute in amounts of 2-3% (mol). The value of α is calculated from the experimental results by means of equation (3)

$$\alpha = \frac{\Delta t}{a} \qquad (3)$$

where α is the depression of the crystallization temperature of cyclohexane caused by addition of 1 mol % solute; Δt - the depression of the crystallization temperature of cyclohexane caused by addition of a known weight of solute; a - the amount of solute added in mol %.

Experimental Determination of the Depression of the Crystallization Temperature of Cyclohexane by Addition of 1 Mol % Solute

It was stated above during consideration of equation (1) that for any given solvent the depression of its initial temperature of crystallization is proportional only to the content of the solute expressed as molar % and is independent of its nature. In order to check this statement experimentally the values of α, i.e., the depression of the crystallization temperature of cyclohexane (used in the method proposed as the solvent) caused by addition of 1 mol.% of different solutes (Table 2), were determined.

The results in Table 2 show that hydrocarbons which have molecular weights similar to that of cyclohexane and which are similar in structure give low values for α, probably as a result of the formation of solid solutions. Thus on addition of methyl cyclohexane the value of α is 1.90 instead of the expected value of 2.42[1], i.e. 21% lower. When benzene was added to cyclohexane the value of α obtained was 2.25 which is 7.6% lower than the calculated value; the value of α obtained by using toluene was 2.34, i.e., 3.3% lower than the calculated value. Hydrocarbons such as n-hexane, and n-heptane which have similar molecular weights to cyclohexane but differ considerably in structure from it give normal values for α. All the other hydrocarbons and mixtures of hydrocarbons tested, differing in structure and with molecular weights varying from 134-291, on addition to cyclohexane depress the crystallization temperature by an average of 2.47. The mean deviation of the values found from the mean was equal to 1.1%, while the maximum deviation (in one case) was 2.8%. The deviation of the mean value of α (2.47) from the calculated value was 2%. It should be noted that errors in determining the molecular weight of a mixture of hydrocarbons by a cryoscopic method in benzene might be a contributory cause for the maximum deviation of 2.8% in one particular case. Analogous results were obtained for four determinations of the cryoscopic constant of cyclohexane when four synthetic mixtures of petroleum fractions boiling between 150-200°, and containing aromatic hydrocarbons were added to cyclohexane. These results are not included in Table 1 so as to save space. The average value of α is 2.44. It can be regarded therefore as experimentally established that the depression of the crystallization temperature of cyclohexane is proportional (with an accuracy of ±3%) to the solute content, but is independent of the nature of the solute, when mixtures of hydrocarbons which have boiling points of 150° and over are used as solutes.

1) The value of α = 2.42 was calculated from the heat of crystallization of cyclohexane (639.3 cal/mol). For further details see [2].

TABLE 2

Depression of the Crystallization Temperature of Cyclohexane by Addition of 1 mol % of Different Hydrocarbons and Mixtures of Hydrocarbons.

No.	Composition of Mixture	Mol. wt.	Depression of $t_{cryst.}$ produced by mol % sol. deg./mol.% (α)
	Calculated on the basis of the heat of crystallization of cyclohexane.	–	2.42
1	n-Hexane	86.2[1]	2.42
2	Benzene	78.1[1]	2.25
3	n-Heptane	100.2[1]	2.45
4	Methylcyclohexane	98.2[1]	1.90
5	Methylbenzene (toluene)	92.1[1]	2.34
6	Diethylbenzene (mixture of isomers)	134.2[1]	2.48
7	A synthetic mixture of 9.4 mol % diethylbenzene and 90.6 mol % decahydronaphthalene	137.8[1]	2.44
8	A synthetic mixture of 82.0 mol % n-hexane and 18.0 mol % 2-phenylheptane	217.4[1]	2.49
9	A synthetic mixture of 29.7 mol % triethylbenzene (mixture of isomers) and 70.3 mol % of n-hexane	207.3[1]	2.44
10	A mixture of alkanes and cyclanes, the 300–350°fraction from Kalinsky petroleum	263[2]	2.50
11	A synthetic mixture of 42.5 mol % of aromatic hydrocarbons (300–350°fraction) and 57.5 mol.% alkanes and cyclanes (300–350°fraction) from Buzovinsky petroleum	250[2]	2.46
12	A synthetic mixture 7.7 mol.% of aromatic hydrocarbons (350–400°fraction) and 92.3 mol.% alkanes and cyclanes (350–400°fraction) from Buzovinsky petroleum.	291[2]	2.40
13	A synthetic mixture of 26.3 mol % aromatic hydrocarbons and 73.8 mol % alkanes and cyclanes (350–400°fraction) from Buzovinsky petroleum.	284[2]	2.45
14	A synthetic mixture of 49.6 mol % of aromatic hydrocarbons (350–400°fraction) from Buzovinsky petroleum and 50.4 mol % of alkanes and cyclanes (350–400°fraction) from the same petroleum.	291[2]	2.40
15	200–250°fraction synthol	176[2]	2.46
16	250–300°fraction synthol	214[2]	2.50

1) Molecular weight calculated on the basis of an empirical formula for the hydrocarbons and their content in the mixture.

2) Molecular weight determined experimentally by a cryoscopic method in benzene.

Checking the Cryoscopic Method on Synthetic Mixtures

The test mixtures as pointed out above were added in amounts of ca.3%. The aromatic hydrocarbons content in the cyclohexane therefore does not usually

exceed 1%. The low concentration of the aromatic hyrocarbons necessitates specific conditions for the H_2SO_4 treatment. It is necessary to remove this small amount of aromatic hydrocarbons completely, while the H_2SO_4 used must not react appreciably with the alkane and cyclane part of the fraction.

One of us with Kurindin [2] showed that monoalkylbenzenes with seven and more carbon atoms in the alkyl group are not completely removed by 98% H_2SO_4, fuming H_2SO_4 with a low concentration of free SO_3 being necessary. As a typical alkylbenzene which is only removed with difficulty by H_2SO_4, we chose 2-phenylheptane.

In order to establish the optimum conditions for H_2SO_4 treatment of the test mixtures in cyclohexane for the elimination of the aromatic hydrocarbons, tests on 14 synthetic mixtures were carried out. The amount of aromatic hydrocarbons in each of these mixtures was determined by the cryoscopic method described above.

Results of these tests (Table 3) showed that the majority of the aromatic hydrocarbons are completely removed by 99.0–99.5% H_2SO_4. However for complete elimination of 2-phenylheptane, fuming H_2SO_4 containing 0.2–0.3% free SO_3 was necessary. For the quantitative determination of aromatic hydrocarbons in petroleum fractions by the cryoscopic method, therefore, we adopted the following H_2SO_4 treatment: 1 hour shaking by hand of equal volumes of fuming H_2SO_4 containing 0.2–0.5% free SO_3 and the cyclohexane solution.

The accuracy of the proposed cryoscopic method for the quantitative determination of aromatic hydrocarbons was tested on 40 synthetic mixtures (Table 4). The mean error was equal to 0.6% (absolute); the maximum error was 2.2% (absolute). The relative % error in calculating the aromatic hydrocarbons varied from 0 to 13% (depending on the hydrocarbon content). The relative mean error was equal to 3.4%.

In order to test the repeatability, experiments, the results of which are not included in the present article, were carried out on the quantitative determination of aromatic hydrocarbons in 7 petroleum fractions. The mean deviation between duplicates amounted to 0.2% (absolute), the maximum deviation was 0.4%.

For a comparison of the proposed cryoscopic method for the determination of aromatic hydrocarbons with the aniline method [3], results are given for both methods in Table 5. The average value of the accuracy of the aniline method given in the table was derived from 7 experiments on synthetic mixtures; these results are not included for the sake of brevity. The relative accuracy of the aniline method (15%) was taken from the literature [4].

The values given in Table 5 show that, as regards accuracy and time spent and also the amount of sample necessary for an analysis, the cryoscopic method has considerable advantages over the aniline method. This is natural since the cryoscopic method is based on a physical law which is independent of the structure of the aromatic hydrocarbons or on the composition of the alkane-cyclane components. The aniline method is of an arbitrary nature and the results obtained when it is used depend on different factors, in particular on the composition of the alkanes and cyclanes composing the test fraction, and on the structure of the aromatic hydrocarbons.

It must be emphasized once again that when the cryoscopic method is used, the value found for the aromatic hydrocarbons content is expressed in mol %, as is usually done in the quantitative determination of unsaturated hydrocarbons by means of iodine and bromine numbers.

TABLE 3

Selection of the Optimum Conditions for H_2SO_4

Test No.	Composition of the Synthetic Mixtures		Conditions of treatment		Aromatic hydrocarbons in mol. %		Deviation Actual–Found	
	Cyclanes, alkanes	Aromatic hydrocarbons	Conc. of H_2SO_4, wt. %	Shaking duration, in min.	Actual	Found	Absolute %	Relative %
1	Cyclane-alkane part of the 200–250° fraction from Kalinsky petroleum.	1-Methylnaphthalene	99.1	60	29.9	29.1	+0.8	+2.7
2	Ditto	2-Phenylheptane	99.5	60	19.5	16.5	+3.0	+15.4
3	Ditto	Triethylbenzene	99.5	60	10.2	9.7	+0.5	+ 4.9
4	Ditto	Triethylbenzene, 1-Methylnaphthalene, 2-Phenylheptane	0.4 free SO_3	30	30.8	30.6	+0.2	+ 0.7
5	Cyclane-alkane part of the 250–300° fraction from Kalinsky petroleum.	Pentamethylbenzene	0.4 free SO_3	30	9.9	10.2	−0.3	− 0.3
6	Ditto	Pentamethylbenzene, Dibenzyl Diamylnaphthalene	0.4 free SO_3	60	41.6	41.5	+0.1	+0.24
7	Cyclane-alkane part of the 300–350° fraction from Kalinsky petroleum.	Diamylnaphthalene	98.0	30	17.6	8.0	+9.6	+54.5
8	Ditto	"	0.1–0.2 free SO_3	30	17.6	17.5	+0.1	+ 0.6
9	Ditto	"	0.1–0.2 free SO_3	60	17.6	17.9	−0.3	− 1.7
10	Cyclane-alkane part of the 350–400° fraction from Buzovinsk petroleum.	Aromatic hydrocarbons from the 350–400° fraction of Buzovinsk petroleum	98.0	30	49.6	19.2	−30.4	−61.3
11	Ditto	Ditto	0.1–0.2 free SO_3	30	49.6	48.7	−0.9	− 1.8
12	Ditto	Ditto	0.1–0.2 free SO_3	60	51.8	50.8	+1.0	+ 1.9

TABLE 4

Checking the Cryoscopic Method for the Quantitative Determination of Aromatic Hydrocarbons on Synthetic Mixtures (amount of H_2SO_4 1 volume)

Test No.	Composition of Synthetic Mixtures		Conditions of H_2SO_4 treatment		Aromatic hydrocarbon content in mol.%		Deviation Actual-Found	
	Cyclanes and alkanes	Aromatic Hydrocarbons	H_2SO_4 conc., % wt.	Length of treatment in min.	Actual	Found	Absolute %	Relative %
1	2	3	4	5	6	7	8	9
1	Decahydronaphthalene	Diethylbenzene	99.1	60	9.4	9.0	+0.4	+5.0
2	Ditto	Ditto	99.1	60	10.2	9.7	+0.5	+5.0
3	"	"	99.1	60	9.9	10.0	−0.1	-1.0
4	"	"	99.1	60	10.0	10.0	0.0	0.0
5	Alkane-cyclane part from the 150-200° fraction of heavy Balakhany petroleum	Diethylbenzene	99.1	60	5.3	4.6	+0.7	+13.0
6	The same mixture	Ditto	99.1	60	5.3	4.6	+0.7	+13.0
7	Alkane-cyclane part of the 150-200° fraction of heavy Balakhany petroleum	"	99.1	60	11.3	10.0	+1.3	+19.0
8	The same mixture	Ditto	99.1	60	11.3	9.9	+1.4	+13.0
9	Alkane-cyclane part of the 150-200° fraction from Bibieibatsky petroleum	"	99.1	60	10.2	10.7	−0.5	- 5.0
10	Ditto	Ditto	99.1	60	32.5	32.2	+0.3	+1.0
11	n-Hexadecane	Triethylbenzene	99.1	60	29.7	29.2	+0.5	+2.0
12	Alkane-cyclane part of the 200-250° fraction from Kalinsky petroleum	1-Methylnaphthalene	99.1	60	29.9	29.1	+0.8	+3.0
13	Ditto	Ditto	0.5% free SO_3	30	29.7	28.9	+0.8	+3.0
14	"	"	Ditto	60	30.0	29.4	+0.6	+2.0
15	"	Triethylbenzene (7.0%) 1-methylnaphthalene (16.9%) 2-paenylheptane (6.9%)	"	30	30.8	30.6	+0.2	+1.0
16	n-Hexadecane	1-Methylnaphthalene	"	30	18.4	18.1	+0.3	+2.0
17	Decahydronaphthalene	Ditto	"	60	19.4	20.3	−0.9	+5.0
18	Alkane-cyclane part of the 250-300° fraction of Kalinsky petroleum	Pentamethylbenzene	"	30	9.9	10.2	−0.3	-3.0

TABLE 4 (continued)

1	2	3	4	5	6	7	8	9
19	Alkane-cyclane part of the 250-300° fraction of Kalinsky petroleum	Diamylnaphthalene	0.5% free SO_3	60	15.2	14.8	+0.4	+3.0
20	Ditto	Pentamethylbenzene	"	60	9.9	10.2	-0.3	-3.0
21	"	Pentamethylbenzene (5.8%), 1,2-Diphenylethane (11.3%), Diamylnaphthalene (24.5%)	"	60	41.6	41.5	+0.1	+0.3
22	Alkane-cyclane part of the 300-350°fraction from Kalinsky petroleum	Diamylnaphthalene	0.1-0.2% free SO_3	30	17.6	17.5	+0.1	+0.6
23	Ditto	Ditto	Ditto	60	17.6	17.9	-0.3	-1.7
24	"	Dicyclohexylindane	"	30	11.5	11.1	+0.4	+3.4
25	"	Ditto	"	60	11.5	11.1	+0.4	+3.4
26	"	Diamylnaphthalene (10.8%), dicyclohexylindane (18%)	"	30	28.8	27.7	+1.1	+3.8
27	"	Ditto	"	30	28.8	28.0	+0.8	+2.8
28	"	"	"	60	28.8	28.1	+0.7	+2.4
29	"	Aromatic hydrocarbons 300-350° fraction from Buzovinsk petroleum	"	30	42.5	42.5	0.0	0.0
30	"	Ditto	"	30	42.5	41.7	+0.8	+1.9
31	"	"	"	30	6.4	6.7	-0.3	+4.7
32	"	"	"	30	6.4	6.5	-0.1	-1.6
33	Alkane-cyclane part of the 360-400°fraction from Buzovinsk petroleum	Aromatic hydrocarbons 350-400° fraction from Buzovinsk petroleum	"	30	49.6	50.5	-0.9	-1.8
34	Ditto	Ditto	"	30	49.6	48.7	+0.9	+1.8
35	"	"	"	30	26.2	28.2	-2.0	-7.6
36	"	"	"	30	26.2	26.9	-0 7	-2.7
37	"	"	"	30	51.8	49.6	+2.2	+4.3
38	"	"	"	60	51.8	50.8	+1.0	+1.9
39	"	"	"	30	7.0	6.9	+0.1	+1.4
40	"	"	"	30	8.6	8.2	+0.4	+4.7
		Mean deviation					0.6	3.4
		Maximum deviation.....					2.2	13.0

TABLE 5

Comparison of the Cryoscopic Method for the Quantitative Determination of Aromatic Hydrocarbons with the Aniline Method

Qualitative Index	Method	
	Cryoscopic	Aniline
Time taken for one analysis	3.5	8
Amount of test fraction necessary for one analysis in ml	0.3-0.5	20
Accuracy of the analysis:		
Absolute %	0.6	2.4
Relative %	3.4	15

SUMMARY

1. A new cryoscopic method has been developed for the quantitative determination of aromatic hydrocarbons in ligroin, kerosene and gas oil fractions of straight distillates.

2. The mean accuracy of the cryoscopic method is 0.6% (absolute) and 3.4% (relative). The average repeatability is 0.2% (absolute).

3. The quantitative determination of aromatic hydrocarbons in one fraction by the cryoscopic method takes 3½ hours, as against 8 hours by the aniline method. The amount of sample necessary for one analysis by the cryoscopic method is 0.3-0.5 ml as against 20 ml for the aniline method.

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A GENERAL METHOD FOR THE INVESTIGATION OF COPRECIPITATION AND ADSORPTION BY MEANS OF LABELLED ATOMS

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During the separation of elements prior to their analytical determination the undesirable phenomena of adsorption and coprecipitation often crop up. These phenomena interfere with the preparation of chemically pure precipitates and often lead to an increased weight of the latter with consequent analytical errors.

Adsorption and cocrystallization are of fundamental importance not only in analytical chemistry but also in a number of industries, e.g. in the separation of radioactive elements from their ores.

The most thorough and fundamental theories of adsorption and coprecipitation during the formation of precipitates were developed by Academician V.G.Khlopin and his school in a series of investigations begun in 1924 [1]. In recent years I.V.Tananaev has devoted a large number of investigations to the application of physico-chemical analysis to systems of analytical importance.

In one of these investigations [2] the solubility of nickel ferrocyanide in the presence of $K_4Fe(CN)_6$, $Na_4Fe(CN)_6$ and $Li_4Fe(CN)_6$ was studied, as well as the chemical composition of the precipitate.

The authors found that under certain conditions the nickel ferrocyanide precipitate during its formation could trap up to 10% of lithium ferrocyanide.

It is possible to determine the solubility of precipitates very simply by means of radioactive indicators using a new method proposed by us recently [3].

The phenomenon of coprecipitation during the formation of precipitates used in analytical practice can also be studied by means of radioactive isotopes.

Thus V.P.Shvedov in checking on the oxalate method of separating calcium from magnesium by means of radioactive calcium concluded that "it is possible to select conditions which lead to a decrease in the coprecipitation of calcium and magnesium, but to eliminate coprecipitation altogether is probably impossible" [4]. The same author in checking the sulfate method of separating calcium and magnesium by means of labelled atoms found that magnesium traps calcium while part of the latter remains in solution [5].

The use of radioactive lead as an indicator enabled V.P.Shvedov in another investigation to propose a method free from coprecipitation for the separation of lead as the oxychloride [6]. Undesirable coprecipitation also occurs in the gravimetric separation of anions.

Thus in the separation of the ortho and pyrophosphates of zinc and cadmium, Van-Straten and Aten using radiophosphorus found coprecipitation occurs to the extent of from 1 to 4% [7].

From the examples already cited it is clear how important adsorption and coprecipitation are for both theory and practical analysis. Insufficient investigation of this problem is undoubtedly connected with the difficulties of the

classical methods when applied to a large number of precipitates formed under various conditions of precipitation.

The use of labelled atoms which could facilitate the solution of these problems has not hitherto been systematically applied to the study of coprecipitation.

The present investigation was undertaken with the aim of developing a general method of studying adsorption and coprecipitation by means of radioactive isotopes. As the object for developing this technique we chose the widely used chromate method of separating barium from strontium.

Checking the Chromate Method

The chromate method for separating barium and strontium was proposed by Fresenius [8] and was subsequently introduced into the text books of analytical chemistry and into a number of All-Union standards.

Before precipitation a few drops of acetic acid are added to the neutral solution of barium and strontium salts and the precipitation in then accomplished by means of ammonium chromate, which according to Fresenius should be "more acid than alkaline". It is recommended that the precipitation be repeated under these conditions. The precipitate A obtained in this way is carefully calcined to constant weight. Strontium is precipitated from the filtrates as carbonate. The latter is dissolved and the strontium subsequently precipitated as the sulfate. This precipitate B is also calcined to constant weight.

Fresenius' method which was modified somewhat by Skrabal and Neustadt [9] was checked recently by Beyer and Rieman [10].

These last authors purely by calculation found that barium chromate should be precipitated at a pH of 4.6.

The precipitates which they obtained under these conditions had reliable weights. The weakness of their work lies in the absence of proof that these precipitates do not contain strontium.

In order to check on this point we carried out a large number of separations according to the Fresenius method, in which the volume of solution was approximately 100 ml in all cases. Results of one series of experiments are adduced in Table 1[1].

TABLE 1

Separation of Barium from Strontium. Results of Gravimetric Determination

No. of expt.	Ba Calc. as $BaCrO_4$			Sr Calc. as $SrSO_4$		
	Taken, in mg	Found		Taken, in mg	Found	
		mg	Percent		mg	Percent
7	62.5	62.8	100.5	46.6	45.8	98.3
8	62.5	64.8	103.5	46.6	44.8	96.0
9	62.5	66.2	106.0	46.6	43.8	94.0
10	62.5	65.8	105.4	46.6	44.0	94.5
11	111.6	137.2	123.5	–	–	–
12	111.6	112.0	100.5	121.0	119.3	98.8

As the results in Table 1 show, gravimetric determination in a number of cases gave completely satisfactory results. In others however even for the determination of barium, inadmissible errors of 3-6% were obtained.

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[1] V.V.Bogacheva carried out a large number of experiments on the precipitation and determination of the activity of the precipitates obtained.

In some cases, as e.g. in experiment 11, the error in the determination of barium exceeded 23%.

In order to explain these deviations, we decided to carry out a number of tests on the separation of barium from strontium by the chromate method using the radioactive isotope Sr^{89}; its characteristics viz a half life of $T_{50\%}$ = 55 days and comparatively hard β-rays make it suitable for this purpose.

Having prepared standards containing a known amount of strontium and comparing its activity with the activity of the precipitates, we could easily determine the actual amount of strontium in the $BaCrO_4$ and $SrSO_4$.

Some results of such determinations are given in Table 2.

In Column 3, Table 2, results are given for the gravimetric determination of $BaCrO_4$ which agree fairly well with the amount of barium actually taken. On the other hand radiometric determinations show that the $BaCrO_4$ contains about 7% $SrCrO_4$. This means, that part of the barium is still in solution and is subsequently precipitated as sulfate together with the strontium.

TABLE 2

Separation of Barium from Strontium. Results of Gravimetric and Radiometric Determinations.

No. of expt.	Amount of barium taken calcd. as $BaCrO_4$, mg	Found in mg			Amount of strontium taken calcd as $SrSO_4$, mg	Found in mg		
		$BaCrO_4$ + $SrCrO_4$	$BaCrO_4$	$SrCrO_4$		$SrSO_4$ + $BaSO_4$	$SrSO_4$	$BaSO_4$
13	62.5	63.8	59.6	4.2	51.6	50.1	47.0	3.1
14	62.5	61.4	57.5	3.9	51.6	51.1	45.7	5.4
15	62.5	63.8	59.9	3.9	51.6	48.3	45.5	2.8
18	62.5	61.4	57.3	4.1	51.6	50.8	45.5	5.6
19	62.5	61.8	57.7	4.1	51.6	50.8	45.6	5.2
20	62.5	62.2	57.7	4.5	51.6	45.8	40.7	5.1

Similar conclusions were reached after determining the specific activity of the $SrSO_4$; the activity was depressed by 6-11%, indicating that a considerable amount of barium accompanies the strontium in the sulfate precipitate. All these relations are shown clearly by consideration of Columns 8 and 9 in Table 2. These experiments showed that the comparatively good results obtained for the determination of barium in the presence of strontium by the Fresenius' method is explained not so much by the merits of the method but by the fortuitous compensation of two errors.

It is obvious that for small variations in the precipitation conditions one should expect a considerable change in the amount of strontium trapped by barium and that this should lead to marked deviations in the analytical results, similar to that deviation which we observed during consideration of Table 1.

It should be interesting to explain whether or not the trapping of stontium is the result of adsorption on the barium chromate precipitate or of coprecipitation. In order to do this we carried out a number of experiments which are described below.

Investigation of the Adsorption of Strontium on $BaCrO_4$

In the experiments on the study of adsorption we precipitated $BaCrO_4$ separately as described above and only afterwards was the solution of $Sr^{89}Cl_2$ poured into the beaker containing the precipitate. The solution and precipitate were mixed

several times in the course of 1 hour, after which the precipitate of $BaCrO_4$ was filtered off, washed, and then calcined to constant weight. The activity of the precipitate was measured with a counter. Results of experiments carried out at different pH values are given in Table 3.

The results in Table 3 show that adsorption of strontium on $BaCrO_4$ in acid, neutral or weak basic solutions does not exceed 1.2%. Only at a pH $\geq$ 9.5 is a sharp increase in activity of the precipitate observed. This is undoubtedly connected with the formation and adsorption of hydrated oxides of strontium of a white color. The relation between adsorption and pH is depicted in Fig. 1 (Curve 6).

TABLE 3

Adsorption of Sr on $BaCrO_4$ precipitates in a solution containing $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$. Activity of the standard I_0 = 2800 impulses/minute

No. of expt.	pH of solution	Activity of ppt., impulses/minute	$\frac{100\ I}{I_0}$
23	6.5	28	1.0
24	8.0	34	1.2
25	8.3	32	1.1
26	9.0	28	1.0
27	9.2	30	1.1
28	9.5	910	32.5
29	9.8	1532	54.7

It is known that in some instances precipitates can be formed during a change in pH as a result of the suppression of the dissocation of the precipitant, in our case chromic acid. However simple calculations on the basis of the soubility product of $BaCrO_4$ ($K_1=2.10^{-10}$) [11] and $SrCrO_4$ ($K_2=4.10^{-5}$) [12] and also of the first dissociation constant of H_2CrO_4 ($K=7.10^{-5}$) [13] show that under the conditions of our experiments the precipitation of $SrCrO_4$ cannot occur in the absence of $BaCrO_4$.

These calculations together with the experiments described above show that the significant trapping of strontium during the formation of $BaCrO_4$ precipitates is explained not so much by adsorption and independent precipitation of strontium, as by its coprecipitation.

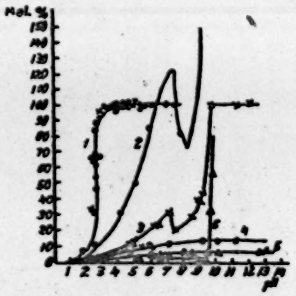

Fig.1. Adsorption and coprecipitation of barium and strontium chromates: 1-precipitation of $BaCrO_4$ from a mixture of $2.46 \cdot 10$ mol/l $BaCl_2$ and $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$ for different pH values. (Circles denote results obtained by measurement of the activity of Ba^{140}, while crosses denote results obtained gravimetrically). Curves for coprecipitation of $SrCrO_4$ with $BaCrO_4$ from solutions containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and different amounts of $SrCl_2$. Curve 2-$12.3 \cdot 10^{-4}$mol/l; Curve 3-$2.51 \cdot 10^{-4}$mol/l; Curve 4-$0.5 \cdot 10^{-4}$ mol/l and Curve 5-$0.25 \cdot 10^{-4}$mol/l; Curve 6-adsorption of Sr on $BaCrO_4$. All results are expressed in mol. percent in relation to the amount of $BaCl_2$ taken.

Investigation of the Coprecipitation of $SrCrO_4$ with $BaCrO_4$

The coprecipitation of strontium and barium was studied in a wide pH range, using the radioisotopes Ba^{140} and Sr^{89} as controls.

The original solution of $BaCl_2$ had a concentration of $2.46 \cdot 10^{-4}$ mol/l. The concentration of $SrCl_2$ in the same solution amounted to $2.51 \cdot 10^{-4}$ mol/l. Precipitation was accomplished either by the Fresenius method as described above or as follows.

To the test solution about 2 ml of 36% HCl is added, followed by an excess of ammonium chromate. When these conditions are observed the hydrogen ion concentration is so high that the barium chromate is not precipitated. Next dilute ammonia (2.5%) was added dropwise to the solution until the requisite pH was obtained. The pH was measured after precipitation of the chromates by means of a pH-meter incorporating a glass electrode.

Comparison of both methods showed that the order of precipitation which we proposed leads to a considerable decrease in the amount of strontium trapped by barium chromate. As a result all the experiments carried out henceforth were made by addition of hydrochloric acid with subsequent neutralization with ammonia instead of Fresenius' method.

In the first series of experiments we used the Ba^{140} isotope and inactive strontium. Having prepared the radiobarium standard and measured the activity of the precipitate at different pH values, we got the results adduced in Table 4.

The results in Table 4 show that precipitates of $BaCrO_4$ on addition of ammonia begin to be formed when the pH $\geq$1. On increasing the pH the percentage of barium precipitated gradually increases and at pH=4.5 complete precipitation of barium is observed.

In all the experiments on coprecipitation, the concentration of $BaCl_2$ was $2.46 \cdot 10^{-4}$ mol/l. All the experiments described below were carried out with Sr^{89}.

TABLE 4

Precipitation of $BaCrO_4$ from solutions containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$. The activity of the standard was I_o=760 impulses/minute.

No. of expt.	pH of solution	Activity of ppt. I, imp./min.	$\frac{100\,I}{I_o}$	No. of expt.	pH of solution	Activity ppt. I, imp/min.	$\frac{100\,I}{I_o}$
30	1.8	57	7.5	46	3.6	746	98.1
31	2.1	20	2.6	47	3.8	756	99.6
38	2.1	18	2.4	48	4.0	726	95.5
32	2.5	240	31.7	49	4.2	745	98.0
39	2.5	480	63.6	57	4.2	764	100.0
43	2.5	500	66.0	50	4.4	758	100.0
33	2.6	465	61.0	58	4.4	738	97.0
40	2.7	351	46.2	52	4.7	762	100.0
41	2.7	514	67.5	53	5.0	760	100.0
44	2.7	630	83.0	54	5.5	741	97.5
34	2.8	669	88.0	59	5.5	760	100.0
42	3.0	697	91.8	55	5.7	752	99.0
45	3.0	510	67.1	56	6.2	759	100.0
35	3.3	745	97.8	60	7.1	763	100.0
36	3.4	744	97.8	61	7.7	762	100.0

In the first series of experiments a concentration of $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$ was employed.

The results of the first series of experiments which was conducted within a wide pH range are given in Table 5.

From a consideration of Table 5 and curve 3, Fig. 1, it can be seen that the first sign of coprecipitation of strontium is observed at pH > 1.5. It is interesting to note that coprecipitation increases up to pH 7.2. On increasing the pH further, coprecipitation at first decreases and then increases again. Minimum coprecipitation occurs at pH ≈7.5.

TABLE 5

Coprecipitation of $SrCrO_4$ with $BaCrO_4$, in a solution containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$.
I_o = 1430 impulses/min.

Expt. No.	pH solution	Activity of ppt. I, imp./min.	100 I / I_o
62	1.8	14	1.0
63	2.3	26	1.8
64	2.7	50	3.5
65	4.2	100	7.0
66	4.9	160	11.2
67	5.0	199	14.0
68	6.3	336	23.5
69	6.5	343	24.0
70	7.3	443	31.0
71	7.6	300	21.0
72	8.5	393	27.5
73	8.9	565	39.5
74	9.1	572	40.0
77	9.2	622	43.5
78	9.9	1432	100
79	11.4	1416	99
80	12.4	1431	100

The second series of experiments was carried out with a solution containing $0.5 \cdot 10^{-4}$ mol/l $SrCl_2$. Results on the determination of the activity of strontium, which increases with formation of $BaCrO_4$ precipitates, are given in the third column of Table 6.

In Column 4, Table 6, the relative amounts of $SrCrO_4$ trapped by $BaCrO_4$ are compared. They are expressed in molar percentages in relation to the amount of $BaCl_2$ taken.

The results of our determinations are depicted in Fig.1, Curve 4.

The third series of experiments was carried out on a solution of $SrCl_2$, the concentration of which was $0.25 \cdot 10^{-4}$ mol/l. Results are given in Table 7 and in Fig. 1 (Curve 5).

In the case just described, as in previous series of experiments, we did not observe a sharp increase in coprecipitation in alkaline solutions. This is explained apparently by the low concentrations of $SrCl_2$, which cannot ensure the formation of a precipitate of hydrated strontium oxide.

The fourth series of experiments was carried out with $SrCl_2$ solution the concentration of which was $12.3 \cdot 10^{-4}$ mol/l, i.e., a molar ratio of Sr:Ba = 5:1.

The results of the experiments carried out with solutions of this concentration are adduced in Table 8 and in Fig. 1 (Curve 2).

In the case of the comparatively concentrated $SrCl_2$ solution the maximum coprecipitation which is observed at pH 7.5 is particularly clearly defined. Consideration of Fig.1, in which results are given for the coprecipitation of strontium with barium chromate for various relative concentrations and at different pH values, enables one to understand why the Fresenius' method gives widely different results for small, practically imperceptible changes in the precipitation conditions.

Precipitation of Barium Chromate at Different pH Values

In order to check the results we carried out a few series of experiments on the separation of barium and strontium by the chromate method. The concentration of the $BaCl_2$ and $SrCl_2$ were $2.46 \cdot 10^{-4}$ mol/l and $2.5 \cdot 10^{-4}$ mol/l respectively. The pH of the solution was determined both before and after formation of the precipitate by means of a pH-meter and glass electrode.

TABLE 6

Coprecipitation of $SrCrO_4$ with $BaCrO_4$ in a solution containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $0.5 \cdot 10^{-4}$ mol/l $SrCl_2$.
I_o = 1620 impulses/min

Expt. No.	pH of solution	Activity of ppt. I, imp/min.	$\frac{100\ I}{5\ I_o}$
81	4.7	406	5.0
82	5.1	403	5.0
83	6.0	721	8.9
84	6.1	648	8.0
85	7.3	906	11.2
86	9.3	1002	13.6
88	10.2	1134	14.0
89	11.3	1100	13.6

TABLE 7

Coprecipitation of $SrCrO_4$ with $BaCrO_4$ in a solution containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $0.25 \cdot 10^{-4}$ mol/l $SrCl_2$.
I_o = 1510 impulses/min

Expt. No.	pH of solution	Activity of ppt. I, imp/min.	$\frac{100\ I}{10\ I_o}$
90	5.1	445	3.0
92	6.0	785	5.2
93	6.4	830	5.5
94	6.6	756	5.0
95	7.1	724	4.8
97	7.6	620	4.1
98	8.5	718	4.6
99	9.5	831	5.5
100	10.6	829	5.5
101	12.6	846	5.6

The precipitate of $BaCrO_4$ containing various amounts of $SrCrO_4$ was filtered, washed and carefully calcined to constant weight (Precipitate A). The filtrate was evaporated and the strontium carbonate (contaminated with barium) precipitate formed thereby filtered off, washed, and dissolved in hydrochloric acid.

TABLE 8

Coprecipitation of $SrCrO_4$ with $BaCrO_4$ in a solution containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $12.3 \cdot 10^{-4}$ mol/l $SrCl_2$.
I_o = 1560 impulses/min

Expt. No.	pH of solution	Activity of ppt. I, imp./min.	$\frac{100\ I}{0.2\ I_o}$
104	4.2	94	30.0
105	5.0	156	50.0
106	5.4	226	72.5
107	7.7	380	75.0
108	8.0	265	85.0
109	8.3	234	75.0
110	9.2	468	150.0
112	9.9	1015	325.0

Ethyl alcohol was then added and the mixture of sulfates precipitated from the solution. The gravimetric determination of these sulfates was carried out by the usual method (Precipitate B).

Using the results adduced in Tables 4-8 and in Fig.1, it is easy to calculate the composition of precipitates A and B.

Results of such calculations and also the results of the gravimetric determinations are compared in Table 9.

The calculated curves expressing the relations between the precipitates A and B and the pH are depicted in Fig. 2. These curves show that the experimental points lie close to the calculated curves.

From a consideration of Fig. 2 it follows that on precipitation from acid solution precipitate A has a small weight, but on precipitation from neutral and alkaline solutions its weight is too much. The weight of precipitate B changes in the reverse direction. Therefore a value of the pH always exists at which a weight of precipitate A can be obtained which corresponds to a complete separation of barium. Of course this precipitate with a "theoretical" weight is really a mixture of $BaCrO_4$ and $SrCrO_4$.

It is obvious that in working out the chromate method for the separation of

TABLE 9

Amounts of $BaCrO_4$ and $SrCrO_4$ Precipitates Calculated from the Precipitation Curves and Found Gravimetrically

Expt. No.	pH	Calculated $BaCrO_4 + SrCrO_4$, in mg	Weight of ppt. A, in mg	Calculated $SrSO_4 + BaSO_4$, in mg	Weight of ppt. B, in mg
115	1.6	1.0	4.5	103.0	99.8
116	2.0	1.6	1.0	102.0	100
117	2.2	2.0	2.3	101.5	99.6
118	2.5	20.0	20.5	90.0	91.7
119	2.6	38.0	38.0	78.0	-
141	2.6	38.0	41.0	78.0	67.0
152	2.6	38.0	42.8	78.0	63.9
120	2.7	52.0	31.6	57.0	75.0
142	2.7	52.0	34.5	57.0	63.2
121	2.7	53.0	52.8	57.0	56.6
143	2.8	56.5	56.5	51.0	50.8
122	3.0	58.7	58.5	48.0	48.5
144	3.2	60.0	60.8	47.0	47.0
123	3.3	60.5	61.2	46.5	-
124	3.6	61.8	61.0	45.8	46.2
125	3.8	62.9	64.0	45.0	44.7
126	4.0	63.5	63.4	44.5	44.5
145	4.1	63.8	63.3	44.0	-
127	4.2	64.0	64.0	43.8	-
146	4.2	64.0	65.9	43.8	42.0
129	4.4	65.0	64.7	43.0	43.4
147	4.4	65.0	65.4	43.0	44.8
130	4.5	65.4	65.4	42.6	42.1
131	4.7	66.0	64.5	41.8	63.2
132	4.8	66.5	66.5	41.5	42.8
133	5.0	67.3	69.0	41.0	40.9
148	5.1	67.8	66.0	40.5	41.7
134	5.2	68.2	67.0	40.0	41.5
135	5.5	69.2	70.0	39.0	38.0
149	5.5	69.2	68.3	39.0	40.3
150	5.5	69.2	71.0	39.0	37.7
136	5.5	69.2	67.7	39.0	40.0
137	6.0	71.0	71.2	37.5	37.6
138	6.4	73.5	73.2	35.0	35.2
139	6.9	76.0	73.5	33.0	36.0
140	7.6	79.0	81.0	30.5	28.4

barium from strontium, as for a number of other similar analytical methods, the efforts of investigators were directed to creating such conditions for precipitation as would ensure obtaining a precipitate of the expected weight. Under these conditions, the precipitate is determined not by the exact pH value of the solution but by more or less approximate procedures for the preparation of the latter.

The chemical perception of good researchers is exemplified by the fact that at the point corresponding to the expected weight of $BaCrO_4$ precipitate (see Fig.2) the solution appears actually to be in accordance with Fresenius' observation "more acid than alkali".

Maximum Coprecipitation

The results which we obtained on the coprecipitation of strontium chromate with barium chromate are characterized by a maximum within a definite pH range.

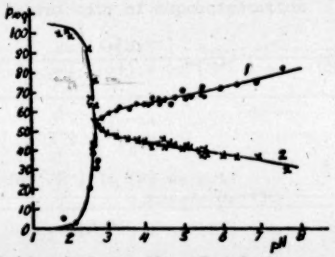

Fig.2. Relation between the pH and the weight of the chromate precipitates A (curve 1) and sulfates B (curve 2) during the separation of barium from strontium.

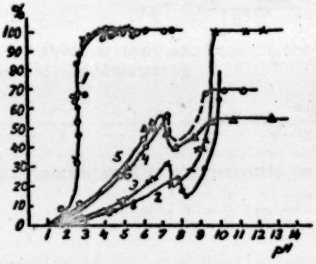

Fig.3. Coprecipitation of $SrCrO_4$ with $BaCrO_4$. All the original solutions contain $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and different amounts of $SrCl_2$: $12.3 \cdot 10^{-4}$ mol/l (curve 2); $2.51 \cdot 10^{-4}$ mol/l (curve 3); $0.5 \cdot 10^{-4}$ mol/l (curve 4) and $0.25 \cdot 10^{-4}$ mol/l (curve 5); Curve 1 shows the precipitation of $BaCrO_4$ for different pH values and curves 2-5 the percentages of $SrCrO_4$ coprecipitated.

This maximum is particularly clearly shown on the coprecipitation pH curve, when the amount of trapped strontium is expressed as a percentage of the amount taken.

Curves of this type are depicted in Fig.3. The pH corresponding to maximum coprecipitation in all cases lies in the 7.2-7.8 range and on an average is equal to 7.5.

The fact that maximum coprecipitation does occur as we have shown can be explained on the assumption that the growth of $BaCrO_4$ crystals proceeds as a result of the transfer of Ba^{++} and CrO_4^{--} ions from solution. Cocrystallization of strontium may proceed only through the stage of adsorption of Sr^{++} ions.

Under these conditions the velocity of strontium coprecipitation is proportional to its adsorption. The latter value according to the Langmuir isotherm is expressed as follows:

$$\theta_{Sr} = \frac{a_{Sr^{++}}[Sr^{++}]}{1 + a_{Sr^{++}}[Sr^{++}] + a_{H}[H^{+}] + a_{OH^{-}}[OH^{-}]} \quad (1)$$

Here θ_{Sr} is the part of the surface of a growing crystal occupied by adsorbed strontium ions; $a_{Sr^{++}}$, $a_{H^{+}}$ and $a_{OH^{-}}$ are the adsorption coefficients for strontium, hydrogen, and hydroxyl ions respectively.

It is clear that the velocity of coprecipitation

$$W = k\,\theta_{Sr} = \frac{k a_{Sr^{++}}[Sr^{++}]}{1 + a_{Sr^{++}}[Sr^{++}] + a_{H^{+}}[H^{+}] + a_{OH^{-}}[OH^{-}]} \quad (2)$$

As is known,

$$[OH^{-}] = \frac{10^{-14}}{[H^{+}]}. \quad (3)$$

Then substituting for $[OH^{-}]$ in (2) we get:

$$W = \frac{k a_{Sr^{++}}[Sr^{++}]}{1 + a_{Sr^{++}}[Sr^{++}] + a_{H^{+}}[H^{+}] + a_{OH^{-}}\frac{10^{-14}}{[H^{+}]}} \quad (4)$$

In order to find the maximum coprecipitation of Sr in relation to hydrogen ion concentration we equate $dW/d[H^{+}]$ to zero. The following equation is then obtained:

$$a_{H^{+}} - \frac{10^{-14} \cdot a_{OH^{-}}}{[H^{+}]^{2}} = 0. \quad (5)$$

It is obvious that maximum coprecipitation of strontium corresponds to the hydrogen ion concentration

$$[H^{+}] = 10^{-7}\sqrt{\frac{a_{OH^{-}}}{a_{H^{+}}}} \quad (6)$$

This concentration corresponds to the value of the pH indicator.

$$pH = 7 + \frac{1}{2}\log\frac{a_{H^{+}}}{a_{OH^{-}}}. \quad (7)$$

According to our experiments, maximum coprecipitation is observed at a pH of approximately 7.5. Substituting the value of the pH in formula (7) we find that

$$\frac{1}{2}\log\frac{a_{H^{+}}}{a_{OH^{-}}} \approx 0.5. \quad (8)$$

This means that if our hypothesis re the mechanism of the crystallization of $SrCrO_4$ is correct then

$$\frac{a_{H^{+}}}{a_{OH^{-}}} \approx 10, \quad (9)$$

i.e., the hydrogen ions are adsorbed practically 10 times better than the hydroxyl ions on the surface of the $BaCrO_4$ crystals.

If the mechanism which we have proposed for coprecipitation is correct the amount of the latter should depend strictly on the concentration of surface active materials in solution.

In this connection we carried out a number of tests in which various amounts of gelatin were added to the solution.

Coprecipitation of Strontium in the Presence of Gelatin

Experiments in which gelatin was added in amounts ranging from 0.001 to 0.03% were carried out with a solution containing $2.51 \cdot 10^{-4}$ mol/l $BaCl_2$ and $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$. Precipitation was carried out either by the Fresenius' method or our method. These experiments showed that when our method is adopted the amount of strontium coprecipitated decreases by 1.5-2 times. All the experiments described below on the precipitation of $BaCrO_4$ in the presence of gelatin were therefore carried out by the addition of hydrochloric acid followed by a gradual neutralization with ammonia.

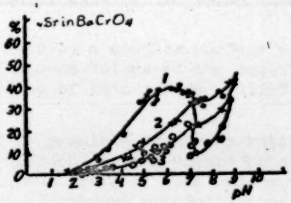

Fig.4, Trapping of strontium during precipitation of $BaCrO_4$ by Fresenius' method (Curve 1), by our method (Curve 2) and by our method in the presence of 0.01% gelatin (Curve 3). In all the experiments the solutions contained $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$.

Our experiments showed that on increasing the concentration of gelatin from 0.001 to 0.01% the amount of strontium coprecipitated gradually decreased. Further increases in the amount of gelatin from 0.01 to 0.03% did not have any effect on the amount of strontium precipitated. It is highly probable that 0.01% gelatin is sufficient for filling up the surface of the growing crystals of $BaCrO_4$. In this connection therefore it is possible to recommend that precipitation of $BaCrO_4$ should be carried out from solutions containing strontium in the presence of 0.01% gelatin.

We carried out comparative experiments of this type on the study of the trapping of strontium during the precipitation of $BaCrO_4$ by Fresenius' method and by our method with and without gelatin.

The results obtained are given in Fig. 4. These curves show that Fresenius' method leads to a considerably higher trapping of strontium than our method does. Coprecipitation is even less when our method is used in conjuction with the use of 0.01% gelatin.

The results which we obtained on the relation between coprecipitation and the concentration of the components of the solution, and other parameters enable the problem of coprecipitation to be considered from the general point of view of physico-chemical analysis.

Physico-Chemical Diagram of Coprecipitation

Physico-chemical analysis was first used by I.V.Tananaev for investigating systems of importance in analytical chemistry. In particular he studied in detail the effect of certain sulfates and nitrates on the solubility of $PbSO_4$. The results enabled him to construct a number of physico-chemical diagrams characterizing the precipitation of lead sulfate under different conditions [14,15,16].

It seems to us that a physicl-chemical diagram on the ordinate of which is plotted a new property "coprecipitation", should play an important part in analytical chemistry. The construction of such diagrams by the classical methods is a

very difficult problem. The method of radioactive indicators as we have shown in the present article allows this problem to be solved fairly easily. Such a method has not hitherto been described in the literature [17].

Two dimensional physico-chemical diagrams of "coprecipitation pH" were given in Figs. 1 and 2. The results which we obtained for coprecipitation at different relative concentrations of Sr/Ba and at different pH values allows a three dimensional physico-chemical diagram of coprecipitation of the type shown schematically in Fig. 5 to be drawn.

The amount of coprecipitation expressed as a percentage of the amount of barium taken is plotted along the vertical axis A while the pH values and the value of Sr/Ba are plotted on the horizontal axis of the three dimensional diagram, respectively

The amount of coprecipitation is characterized by a complex surface with a crest and a hollow corresponding to maximum and minimum values of the amount of strontium in the precipitate. The spatial disposition of this surface relief is also shown by a consideration of Figs. 5 and 6.

By means of the coprecipitation diagram it is possible to choose rationally conditions for subsequent precipitation of $BaCrO_4$ such as will ensure obtaining a precipitate of the requisite purity with a minimum waste of time and labor. To achieve this end it is necessary to carry out subsequent precipitations under those conditions where the line of the process corresponds to a minimum coprecipitation of strontium for complete precipitation of barium. As shown in Fig. 1, this condition is observed at a pH of 5. The value of the pH should be controlled by means of a pH meter.

If precipitation is carried out by Fresenius' method in equimolar solutions at a pH of 5, about 30% of strontium is trapped.

The order of precipitation proposed by us (addition of hydrochloric acid and gradual neutralization with ammonia) decreases the amount of strontium trapped to 12%.

Finally our method in conjuction with the use of 0.01% gelatin lowers the amount of strontium coprecipitated to 6%.

It is possible by using a physico-chemical diagram of coprecipitation to start with a solution containing equivalent amounts of barium and strontium and, by precipitating twice, separate barium containing less than 1% strontium completely, and get complete agreement with theory.

To get such a result by means of the old empirical method would necessitate not less than 4 reprecipitations.

The method of investigating coprecipitation with the aid of radioactive isotopes is of a general character and can be applied for investigating a large number of different systems which are important in analytical chemistry.

SUMMARY

1. A general method has been worked out for investigating coprecipitation by means of radioactive indicators.

2. The relation of coprecipitation of $SrCrO_4$ and $BaCrO_4$ to their relative concentrations and at different pH values has been studied.

3. Maximum coprecipitation was found to occur at a definite pH.

4. A new property is introduced into physico-chemical analysis, "coprecipitation", and a three dimensional diagram is constructed for the coprecipitation of strontium chromate and barium chromate.

5. By means of the three-dimensional physico-chemical diagram of coprecipitation, improvements are introduced into the chromate method for the separation of barium from strontium.

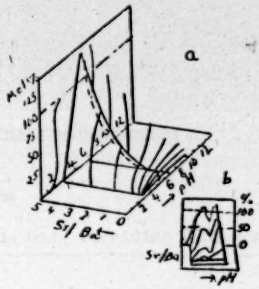

Fig. 5. Three-dimensional diagram of coprecipitation of Sr and $BaCrO_3$ at different values of Sr/Ba and pH.

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A COLOR REACTION FOR FLUORIDE IONS USING TITANIUM-CHROMOTROPIC ACID REAGENT

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It is well known that the fluoride ion does not form colored compounds. In order to determine fluorides colorimetrically therefore their property of decolorizing colored compounds of certain metals is used. The complexes of zirconium or thorium with alizarin, ferric thiocyanate and the compound of titanium with hydrogen peroxide are most often used as the colored complexes. The determination of fluorides by means of zirconium and thorium complexes and also of iron cannot be carried out in the presence of sulfates and phosphates, since these anions give rise to practically the same decolorizing effect as the fluoride ion.

This drawback of course is connected with the use of zirconium, thorium, and iron and cannot be eliminated by the substitution of the alizarin or thiocyanate complexes with some other colored compounds of these metals.

The drawback of the peroxide compound of titanium as a reagent for fluorides is the low sensitivity of the reaction which is determined by the weak color of the titanium peroxide. The sulfate ions do not interfere appreciably because they do not form stable complexes with titanium. Phosphates in small amounts also do not interfere with the determination. In order to detect fluoride ions, therefore, it is expedient to use colored complex compounds of titanium, which, however, have a higher molar concentration of absorption than titanium peroxide complexes.

The Sensitivity of Reactions for the Fluoride Ion Using Certain Colored Complexes of Titanium

The most characteristic expression of the sensitivity of a color reaction is the molar coefficient of absorption of colored compounds. Results are given in the diagram of absorption curves for certain colored complexes of titanium with a series of reagents such as hydrogen peroxide (Curve 1); alizarin (2); pyrocatechol (3), tannin (4), chromotropic acid (5). The curves were obtained by measuring the absorption by means of an FM photometer fitted with various light filters. The solutions were prepared as follows: in all cases a ten-fold excess of reagent of reagent with respect to titanium was used. This ensures that the titanium is all combined as the complex. The concentrations of the colored solutions with respect to titanium was always 0.0002 M with the exception of the peroxide compounds. In the case of the peroxides 0.1 M solution with respect to titanium was used. The pH of the solution was 1 (for the peroxides) and 3 for the remainder. The results adduced in the diagrams show that of the groups studied the most sensitive reagent for titanium is chromotropic acid. The molar coefficient of absorption of the titanium-chromotropic acid complex was roughly 100 times that of the peroxide compound of titanium.

The colored compound of the metal can be used as a reagent for the fluoride ion only when the fluoride complex of the metal under certain conditions is more stable than the colored complex of this metal.

In order to solve this question for the titanium complexes indicated above, the following experiments were carried out. The minimum amount of sodium fluoride necessary for half decolorizing the given complex was determined, the concentration of complexes being selected so that the intensity of their colors was approximately equal. Each solution was divided up into two lots of 10 ml each. One lot was diluted by the addition of an equal volume of water, while the other lot was titrated with 0.02 M sodium fluoride solution from a microburet until the colors of the first and second lots were the same. The results are given in the Table.

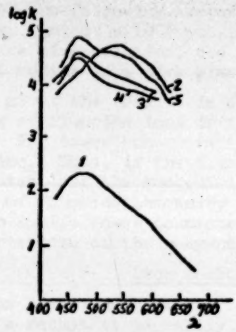
It was found that the titanium-chromotropic acid reagent needed the smallest amount of sodium fluoride. Thus, the most suitable reagent for the fluoride ion is this complex of titanium and chromotropic acid, which satisfies the above conditions.

Effect of pH on the Color Intensity of the Titanium-Chromotropic Acid Complex

In order that solutions of titanium salts should not hydrolyze they should contain excess mineral acid. The pH of the solution, however, affects the color intensity of the titanium-chromotropic acid complex. In strong acid media a compound is formed which is colored bright red, the intensity of the color increasing on increase of the pH until a maximum is reached at a pH of 3. On increasing the pH further (pH 5), the solution changes color. The red complex acquires a yellow color, which is not decolorized on the addition of fluorides. A pH of 3 is therefore the optimum. The necessary hydrogen ion concentration is attained by use of a buffer of monochloracetic acid and its salts. In the following experiments we used a 0.1 N solution of monochloroacetic acid, half neutralized with 0.1 N alkali. The pH of this mixture is 2.85.

Increasing the Sensitivity of the Reaction and Preparation of the Reagent for the Color Reaction

In the presence of fluoride ions the red color of the titanium-chromotropic acid complex weakens as a result of the formation of the complex ion $[TiF]^{3+}$ or $[TiOF]^{+}$. The free chromotropic acid which separates out during this reaction is practically colorless. Thus, the presence of fluorides leads to a weakening of the color. It is accepted that the eye is far more sensitive to change in color that to a weakening of the color. The change in color will be more evident if a blue dye which is stable in acid media such as methylene blue is added to the solution of the titanium-



Reagent	Conc. of titanium, in mol.	Conc. of reagent, in mol.	Amount of 0.02 mol NaF, necessary for decolorization of solution by 50%, in ml.
Chromotropic acid	10^{-3}	10^{-3}	0.2
Tannin	10^{-3}	1%	0.3
Pyrocatechol	10^{-3}	10^{-3}	0.4
Alizarin	10^{-3}	10^{-3}	0.6
Hydrogen peroxide	$2,5 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	0.8

chromotropic acid complex. The mixture of this dye with the red titanium-chromotropic acid complex has a brown color. On addition of fluoride ions a fairly sharp change in the color of the solution from brown to blue can be observed. This enables very small changes in the color of the solution to be observed and increases the sensitivity of the reaction.

PROCEDURE

Reagent.

1) Solution of titanium sulfate; 1.6 g of the basic titanium sulfate $TiOSO_4$ is dissolved in 50 ml sulfuric acid (1:1) with heating. The solution is diluted with water and the titanium hydroxide precipitated with ammonia. This precipitate is filtered, washed, and dissolved in 50 ml of 1.5 mol/l sulfuric acid. The volume of solution is made up to 100 ml with the same acid solution. An approximately 0.1 M solution of titanium sulfate is thus obtained. The exact strength is determined gravimetrically. This solution serves as the base solution for making up less concentrated solutions.

2) A solution of chromotropic acid (1,8-dihydroxynaphthalenesulfonic acid) is prepared by dissolving 0.4 g of the dry compound in 1 liter of water. On standing the solution darkens; it is better therefore to use freshly prepared reagent.

3) A 0.01% solution of methylene blue in water.

4) Buffer solution. 0.945 g of monochloracetic acid is dissolved in 100 ml of water (0.1 mol/l solution). 25 ml of this solution is titrated with 0.1 N NaOH using phenolphthalein. To the remaining solution of monochloracetic acid 0.1 N alkali is added so that the solution is half neutralized. The pH of the final

solution is equal to pK for monochloroacetic acid (2.85).

For the determination of fluorides in solution a reagent is prepared which includes the following components; 5 ml of a 10^{-2} mol/liter solution of titanium sulfate, 1 ml of a 10^{-3} mol/liter solution of chromotropic acid, 1 ml of the methylene blue solution, and 1 ml of the buffer. The reagent can be stored for several months in a dark place.

1 ml of the reagent is added to 1-2 ml of the test solution. The presence of 4 µg of fluoride ions in this volume gives rise to an immediate change in color. For lower concentrations of fluoride the color change only occurs after some time. Thus, if the fluoride content is 0.- µg, the color changes after 10-15 minutes. If the reagent is used without a dye (methylene blue), the minimum amount of fluoride necessary to cause an observable change in color amounts to 4 µg in 2 ml. Lower concentrations even after long standing cause no appreciable decolorization of the reagent.

Drop Technique for Carrying Out the Reaction

The titanium-chromotropic acid complex is only weakly fixed by filter paper, and as a result it is easily washed off by plain water, while decolorization of the spot occurs. It is more convenient to use the drop technique on cellophane. For this purpose the cellophane is given a preliminary treatment in the course of 1 hour with 10% alkali at 50°. The cellophane, when treated in this way, is easily colored by the reagent mixture consisting of the following components: 1 ml 0.01 mol/liter titanium sulfate, 1 ml of 0.01% methylene blue, and 0.01 g chromotropic acid (added in the dry state so as not to dilute the solution). The cellophane is immersed in this solution for 5-8 minutes and then withdrawn; drops of liquid are removed with a filter paper, and the cellophane dried in the air. Cellophane test papers can be stored for several months in a closed vessel in the dark.

The cellophane test paper has a reddish-brown color; if a drop containing fluoride ion is placed on it, a blue spot appears. It should be noted that the chromotropic acid complex, though only slowly, is nevertheless eventually washed off the cellophane by water. Therefore, if the change in color of the spot takes a long time (20 minutes and more) the reaction cannot be regarded as conclusive. The sensitivity of the reaction is 1 µg and the limiting dilution 1:50,000.

Effects of Other Ions

Sulfates, even in large amounts do not interfere. Phosphates cause a change in the color of the reagent in the same way as fluorides; nevertheless, the change as the result of phosphate action is much slower. It was established that 0.01 mol/liter of a phosphate solution in the course of 5 minutes decolorizes the reagent mixture to the same extent as 0.001 mol/liter sodium fluoride solution.

The sensitivity of the titanium-chromotropic acid reagent towards silicofluorides (fluosilicic acid and silico tetrafluoride) is the same as to the fluorides.

SUMMARY

1. A new color reaction for the fluoride ion is proposed which is based on the use of a titanium-chromotropic acid complex, and by means of which 0.2-2 mg/liter of fluoride ion can be detected.

2. The reaction can be carried out by a drop technique on cellophane. The sensitivity is 1 µg of fluoride ion at a limiting dilution of 1:50,000.

3. The reaction can be carried out in the presence of large amounts of sulfate, but in the presence of phosphates the reaction is not reliable.

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QUANTITATIVE ANALYSIS OF GLASSES OF THE SYSTEM $Na_2O - CaO - SiO_2$ ON THE BASIS OF THEIR PHYSICO-CHEMICAL PROPERTIES

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In our article on "Quantitative Analysis on the Basis of the Physico-Chemical properties of the Components" [1] we aimed at indicating the possibility of quantitative physico-chemical analysis of the components of this system, in which we confined ourselves to introducing one interpolated equation embracing a family of curves depending on one parameter for each property. In this way the problem resolved itself into a solution of linear equations.

In the present article in order that the practical side may be simplified we propose a graphical representation of the individual properties (Figs. 1 and 2), so that composition can be determined from a consideration of the points of intersection of lines representing equal properties.

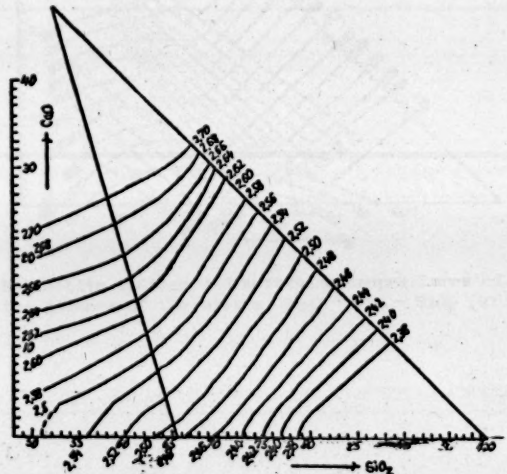

Fig. 1. Density of glasses of the system $Na_2O - CaO - SiO_2$ (wt.%).

[1] Proceedings of the Commission on Analytical Chemistry, Vol.8, 1952

Thus on one triangular diagram we plot softening temperatures and refractive indices and on the other the specific gravities for the same compositions; the point of intersection can be found by superposing transparent paper copies of the two diagrams on each other. In order to widen the scope and increase the accuracy of the analysis, we used 8 interpolated equations as the basis of our calculations for the families of curves corresponding to these three properties.

It should be noted that if the experimental results used as the basis of calculations are not reliable enough in some cases it might be necessary to resort to the method of least squares for calculation.

As examples we adduce comparisons of the compositions as determined by analyses with those calculated on the basis of physico-chemical properties. Results are given in tabular and graphical form.

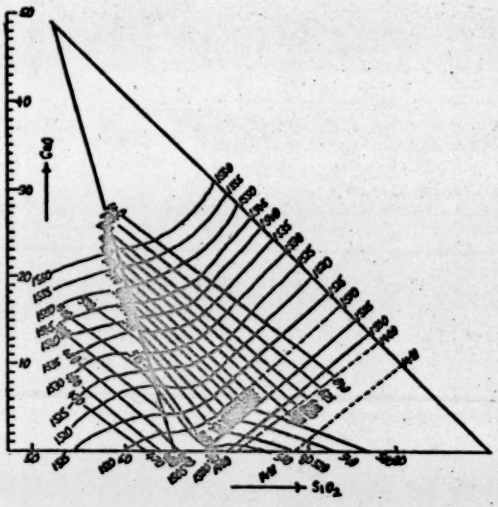

Fig.2. Refractive indices and softening temperatures of the glasses of the system $Na_2O - CaO - SiO_2$ (wt. %).

TABLE

Analyzed composition in percent		Physico-chemical constants of the composition Na_2O, CaO, SiO_2.	Components in percent calculated on the basis of:		
			n and t	n and d	average composition
Na_2O	22.5		22.0	23.1	22.6
CaO	9.5		9.6	9.2	9.4
SiO_2	68		68.4	67.7	68
		n=1.523; t=560° d=2.533			
Na_2O	16.4		17.4	16	16.7
CaO	3.3		2.8	3.6	3.2
SiO_2	80.3		79.8	80.4	80.1
		n=1.4935; t=560° d=2.3886			
Na_2O	15.2		15.5	14.7	15.1
CaO	10.7		11	10.3	10.7
SiO_2	74.1		73.5	75	74.2
		n=1.5182 t=600° d=2.4935			
NaO_2	15.2		16.1	14.1	14.9
CaO	9.3		9.2	10.1	9.6
SiO_2	75.5		74.7	75.8	75.3
		n=1.5135; t = 600 d=2.4734			
Na_2O	21.2		21.1	21.8	21.5
CaO	14.6		14.1	14.2	14.1
SiO_2	64.2		64.8	64	64.4
		n=1.536; t=570° d=2.5851			
Na_2O	21.7		21.5	21.8	21.8
CaO	11.8		11.8	11.7	11.7
SiO_2	66.5		66.5	66.5	66.5
		n=1.529; t=560° d=2.5564			
Na_2O	23		23.8	22.6	23.1
CaO	6.6		6.2	6.7	6.4
SiO_2	70.5		70	70.7	70.4
		n=15145; t=545° d=2.498			
Na_2O	37.5		37.1	37.9	37.5
CaO	5.8		6.2	5.9	6
SiO_2	56.7		56.7	56.2	56.5
		n=15238; t=480° d=2.572			
Na_2O	34		33.6	33.4	33.5
CaO	9.8		10	10.1	10
SiO_2	56.2		56.4	56.5	56.5
		n=15320; t=495° d=2.5976			

TABLE (Continued)

Analyzed composition in percent		Physico-chemical constants of the composition Na_2O, CaO, SiO_2.	Components in percent calculated on the basis of:		
			n and t	n and d	average composition
Na_2O	17.8		17.2	18.2	17.7
CaO	16		16.3	16	16.1
SiO_2	66.2		66.5	65.8	66.2
		n=1.540; t=595° d=2.591			
Na_2O	20		19.7	20.2	19.9
CaO	20		20	20	20
SiO_2	60		60.3	59.8	60.1
		n=1.5535; t=580° d=2.657			
Na_2O	12.3		12.3	10.4	11.2
CaO	13.1		13.1	14.6	13.6
SiO_2	74.7		74.7	75.5	75.2
		n=1.5211; t=627° d=2.496			

SUMMARY

1. The practice of quantitative physico-chemical analysis can be considerably simplified by graphical representation of individual properties.

2. The accuracy of the analysis of the components of a complex system can be considerably increased by increasing the number of the interpolated equations.

Received March 12, 1952

THE QUANTITATIVE DETERMINATION OF TRIVALENT IRON BY MEANS OF TETRABORATE

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Existing methods for the quantitative determination of trivalent iron for the most part consist essentially in reducing it to the bivalent stage when it is titrated with different oxidizing agents [1,2,3,4].

Very little light has been thrown on the direct determination of trivalent iron [5,6]. The development of a direct method is a very important practical problem.

Shchigol's investigations have shown that soluble salts of aluminum, chromium and other elements react easily and quantitatively with the tetraborate ion to form new complex compounds of the composition $[MeB_4O_7]^+$ or $[Me(BO_2)_2B_2O_3]$ and $[Me_2(B_4O_7)_3]$ or $[Me_2(BO_2)_6 \cdot 3B_2O_3]$. We found that ferric ions in dilute solutions also react quantitatively with tetraborate to form similar complex iron borates.

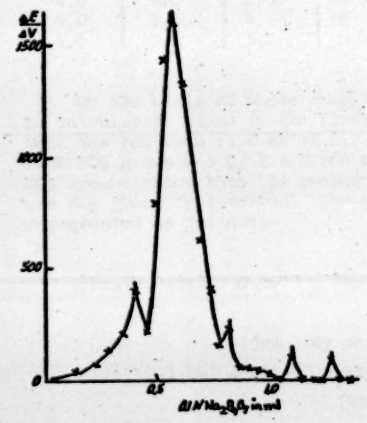


Fig. 1. Titration of 1 ml 0.057 N $FeCl_3$ with 0.1 N $Na_2B_4O_7$.

During the potentiometric titration of aqueous solutions of ferric chloride, the brown titration mixtures gradually acquire a yellow-orange color. One drop in excess of borate after the equivalence point leads to the formation of a precipitate which is obviously the result of the break down of a complex. A number of potential jumps are observed on the titration curve (Fig.1); the first – a small one – represents a compound in which 1 g-ion of iron corresponds to 1 g-ion of tetraborate $[FeB_4O_7]^+$, the second – a large one – is of practical significance and represents an equivalence point at which 2 g-ion of iron corresponds to 3 g-ion of tetraborate $[Fe_2(B_4O_7)_3]$ $\left(E_{Fe} = \frac{M}{3}\right)$. The reaction proceeds according to the following equation.

$$2Fe^{3+} + 3B_4O_7^{2-} \rightleftarrows [Fe_2(B_4O_7)_3].$$

The third, fourth, and fifth potential jumps indicate a gradual break down of the complex compound with the formation of basic salts and finally of ferric hydroxide. According to the extent of the decrease in concentration of the titrated iron salt the jump increases.

It is pertinent to speculate on the nature of these potential jumps after the equivalence point.

In order to answer this question the following experiments were carried out; 2 ml of 0.08 N $FeCl_3$ solution was placed in a 25 ml standard flask and 10 ml water and 1.6 ml of 0.1 N $Na_2B_4O_7$ solution added. The mixture was heated on a water bath until a completely clear solution was obtained. On cooling, an excess of borate was added; for the first experiment $^1/_3$ of the initial amount of borax was added (0.52 ml of the 0.1 N solution, i.e., $^1/_3$ of 1.6 ml); for the second $^2/_3$ (1.04 ml); and for the third $^3/_3$ (1.6 ml). The respective solutions were then made up to the mark with water and filtered. 10 ml of the filtrate in the presence of the same volume of glycerol was titrated with 0.1 N NaOH using phenolphthalein as indicator. The results of some of these experiments are given in Table 1.

TABLE 1

$FeCl_3$	Amount of 0.1 N solution taken, in ml		0.1 N NaOH, in ml		Amount, in ml, of 0.1 N BO_2^- in the basic salt	Number of BO_2^- groups in basic salt
	$Na_2B_4O_7$ initial	$Na_2B_4O_7$ excess	Reqd.	Excess		
1.6	1.6	0.52	3.72	3.30	0.42	2
1.6	1.6	1.04	4.24	3.96	0.28	1
1.6	1.6	1.5	4.8	4.73	0.07	–
4.0	4.0	1.34	9.34	8.04	1.3	2
4.0	4.0	2.68	10.68	10.12	0.56	1
4.0	4.0	4	12	11.90	0.1	–
1.6	1.6	3.2	6.4	6.1	0.3	1

On the basis of these results the number of BO_2^- groups in the basic salt can be calculated. Thus in the first experiment for each BO_2^- group 0.266 ml of 0.1 N NaOH was required (1.6 ml of 0.1 N $Na_2B_4O_7$ is equivalent to 3.2 ml of 0.1 N BO_2^-; each BO_2^- group = 3.2/12 = 0.266 ml 0.1 N NaOH). Thus in the first experiment two BO_2^- groups enter into the composition of the basic iron salt, while in the second, one BO_2^- group is involved. The equations for these reactions can therefore be represented as follows:

$$[Fe_2(B_4O_7)_3] + B_4O_7^{2-} + 8H_2O \longrightarrow Fe\begin{matrix}(BO_2)_2\\OH\end{matrix} + Fe(OH)_3 + 2BO_2^- + 12HBO_2;$$

(3rd jump on the curve in Fig. 1)

$$[Fe(BO_2)_2OH] + B_4O_7^{2-} + 2H_2O \longrightarrow Fe(BO_2)(OH)_2 + 2BO_2^- + 3HBO_2;$$

(4th jump)

$$[Fe(BO_2)(OH)_2] + B_4O_7^{2-} + 2H_2O \longrightarrow Fe(OH)_3 + 2BO_2^- + 3HBO_2.$$

(5th jump)

The last experiment shows that ferric hydroxide reacts with boric acid to form a basic salt possibly as follows:

$$2Fe(OH)_3 + B_4O_7^{2-} \longrightarrow Fe(OH)_3 \cdot Fe(BO_2)(OH)_2 + 2BO_2^- + HBO_2.$$

It should be pointed out that the basic borates of iron were synthesized and studied by Rose [7]; he ascribed to them the formulas $4Fe_2O_3 \cdot 3B_2O_3 \cdot 9H_2O$ or $6Fe(BO_2)(OH)_2 \cdot 2Fe(OH)_3$. In addition the basic borates occur in nature as minerals

such as fonsenite $Fe_2O_3 \cdot B_2O_3$ and also enter into the composition of Indersk borates which are found in the USSR.

In order to study the complex iron borates further these salts were potentiometrically titrated with 0.1 N HCl and $H_2C_2O_4$ in aqueous alcohol. The titration is represented in Fig.2. When HCl is used, 3 potential jumps can be observed on the titration curve according to the number of B_4O_7 groups composing the internal sphere of the complex. The reaction proceeds as follows:

$$[Fe_2(B_4O_7)_3] + 2HCl + 5H_2O \longrightarrow [Fe_2(B_4O_7)_2Cl_2] + 4H_3BO_3,$$

$$[Fe_2(B_4O_7)_2Cl_2] + 2HCl + 5H_2O \longrightarrow [Fe_2(B_4O_7)Cl_4] + 4H_3BO_3,$$

$$[Fe_2(B_4O_7)Cl_4] + 2HCl + 5H_2O \longrightarrow [Fe_2Cl_8] + 4H_3BO_3.$$

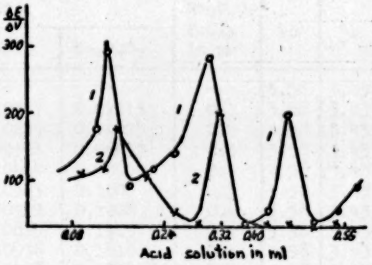


Fig.2. Titration of 1 ml 0.048 N complex with 0.1 N HCl (Curve 1); the same with 0.094 N $H_2C_2O_4$ (Curve 2).

When oxalic acid is used for titration, only two jumps are observed. The third jump is absent. This may be explained if it is assumed that $[Fe_2(B_4O_7)_3]$ is a multinuclear complex compound $[FeB_4O_7][Fe(B_4O_7)_2]$. Obviously in this case only two so called "anionic" groups of $B_4O_7^{2-}$ are titrated; the cationic group $B_4O_7^{2-}$ does not titrate since in all probability the instability constant of $[Fe(B_4O_7)]^+$ is less than or equal to that of $[FeC_2O_4]^+$.

In order to determine the instability constant of the iron borates we studied the equilibrium in the systems $[Fe_2(B_4O_7)_3]$ – KSCN and $[Fe_2(B_4O_7)_3]$ – CH_3COONa. The instability constants for $[FeCNS]^{++}$ and $\left[Fe\begin{matrix}Ac_2\\H_2O\end{matrix}\right]^+$ have been determined by Babko [10,12]. This in conjunction with the experimentally determined equilibrium constant enables the instability constants of the iron borates to be calculated.

$$K_p = \frac{K^2[FeCNS]^{2+}}{K_{[Fe_2(B_4O_7)_3]}}.$$

The average value of $K_{[Fe_2(B_4O_7)_3]}$ is $0.7 \cdot 10^{-12}$, while $K_{[FeB_4O_7]^+} = 1.78 \cdot 10^{-17}$.

Of a number of other physico-chemical methods of investigating complex compounds in solution we used the cryoscopic and specific electro-conductivity methods for the system $FeCl_3$ – $Na_2B_4O_7$.

Cryoscopy as a physico-chemical method of analysis was proposed by Fialkov and Muzika [8] and is based on the fact that in a system where complex formation occurs, the amount of particles in solution is not additive, but depends on the

composition and properties of the complex. The change in the number of particles as a result of the formation of a new compound should be reflected in the extent of the depression. Aqueous solutions of the $FeCl_3$– $Na_2B_4O_7$ system were subjected to test. The procedure was as follows: to an aquous solution of $FeCl_3$ was added a gradually increasing amount of borax and the freezing point determined. The Beckmann method was used. Since on interaction of $FeCl_3$ and $Na_2B_4O_7$ an equivalent amount of NaCl is formed which affects the freezing point of the system, preliminary freezing point measurements were made on aqueous solutions of the system $FeCl_3$ – NaCl where the variable was NaCl. Results are given in Table 2 and Fig. 3.

TABLE 2

Weight in g				$Na_2B_4O_7$ / $FeCl_3$ in mol.	t_0	t_1	t_2	t_3	Δt
H_2O	$FeCl_3$	NaCl	$Na_2B_4O_7$						
50.03	0.162	–	–	–	3.58	3.43	–	–	–
50.03	0.162	0.0117	0.02013	0.1	3.58	3.43	3.415	3.39	0.025
50.03	0.162	0.0234	0.04025	0.2	3.58	3.43	3.400	3.36	0.040
50.03	0.162	0.0351	0.06037	0.3	3.58	3.43	3.385	3.34	0.045
50.03	0.162	0.0468	0.08050	0.4	3.58	3.43	3.370	3.33	0.040
50.03	0.162	0.0585	0.1006	0.5	3.58	3.43	3.335	3.31	0.045
50.03	0.162	0.0702	0.1208	0.6	3.58	3.43	3.340	3.29	0.050
50.03	0.162	0.0819	0.1409	0.7	3.58	3.43	3.325	3.28	0.045
50.03	0.162	0.0936	0.1610	0.8	3.58	3.43	3.310	3.26	0.050
50.03	0.162	0.1053	0.1812	0.9	3.58	3.43	3.295	3.24	0.055
50.03	0.162	0.1170	0.2014	1	3.58	3.43	3.280	3.21	0.070
50.03	0.162	0.1287	0.2215	1.1	3.58	3.43	3.260	3.20	0.060
50.03	0.162	0.1404	0.2416	1.2	3.58	3.43	3.250	3.17	0.080
50.03	0.162	0.1521	0.2617	1.3	3.58	3.43	3.235	3.15	0.085
50.03	0.162	0.1638	0.2818	1.4	3.58	3.43	3.220	3.13	0.090
50.03	0.162	0.1696	0.2919	1.45	3.58	3.43	3.210	3.13	0.080
50.03	0.162	0.1725	0.2970	1.47	3.58	3.43	3.205	3.13	0.075
50.03	0.162	0.1842	0.3171	1.57	3.58	3.43	3.420	3.13	0.297

Notes.
t_0 - freezing point of water
t_1 - freezing point of an aqueous solution of $FeCl_3$
t_2 - freezing point of an aqueous solution of the system $FeCl_3$ – NaCl
t_3 - freezing point of aqueous solution of the system of $FeCl_3$– $Na_2B_4O_7$
Δt - depression of the complex ($t_2 - t_3$)

The results obtained show that two minima are observed on the depression curve which correspond to molar ratios of $FeCl_3$:$Na_2B_4O_7$=1:1 and 1:1.5, which confirms the formation in solution of complex borates of the compositions $[FeB_4O_7]^+$ and $[Fe_2(B_4O_7)_3]$.

Measurements on the specific electroconductivity of the system were carried out at 25 and 40° in a concentration range of from 0 to 61.4 mol. % borax. For this purpose a series of solutions was prepared in which gradually increasing amounts of borax (from $2\cdot10^{-3}$ to $2\cdot10^{-2}$ mol/l) were added to a constant amount of $FeCl_3$. The specific electroconductivity of equivalent amounts of NaCl formed by the interaction of $FeCl_3$ and $Na_2B_4O_7$ was taken into account. Results are given in Table 3 and Fig 4. These physico-chemical investigations of the system $FeCl_3$ – $Na_2B_4O_7$ show convincingly that ferric ions in aqueous solutions react with the tetraborate ion to form multi-nuclear complex compounds of the composition $[FeB_4O_7]^+$ or $[Fe(BO_2)_2B_2O_3]^+$ and $[Fe_2(B_4O_7)_3]$ or $[Fe_2(BO_2)_6\cdot3B_2O_3]$.

This served as a basis for developing a new method for the quantitative determination of ferric ions both in the free state or in admixture with other ions.

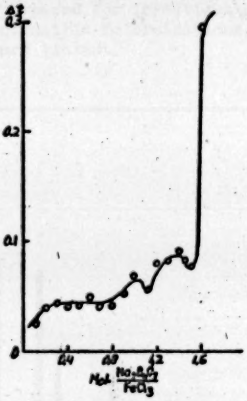


Fig. 3 Cryoscopy of the $FeCl_3 - Na_2B_4O_7$ system.

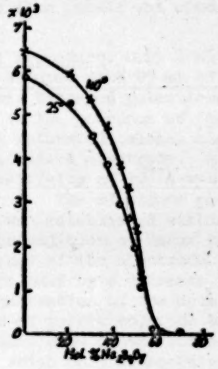


Fig. 4 Specific electroconductivity of the $FeCl_3 - Na_2B_4O_7$ system.

TABLE 3

$Na_2B_4O_7$, in mol. %	$\chi \cdot 10^3$ at 25°			$\chi \cdot 10^3$ at 40°		
	$FeCl_3 - Na_2B_4O_7$	NaCl	Complex	$FeCl_3 - Na_2B_4O_7$	NaCl	Complex
-	5.39	-	-	6.50	-	-
22.4	6.31	0.927	5.38	7.12	1.35	5.77
30.3	5.87	1.3	4.57	7.12	1.74	5.38
36.7	5.75	1.84	3.91	6.92	2.18	4.74
42.0	5.32	2.23	3.09	6.67	2.80	3.87
46.5	5.309	2.64	2.68	6.52	3.17	3.35
50.3	5.053	3.17	1.98	6.07	3.78	2.29
53.6	4.50	3.40	1.10	5.51	4.22	1.29
57.1	4.20	4.00	0.20	4.84	4.60	0.24
59.9	4.50	4.37	0.17	5.40	5.43	0
61.4	4.60	4.65	0	5.50	5.60	0

The choice of an indicator electrode plays an important role in the potentiometric method for the determination of ferric iron described below. A platinum plate covered with a thin layer of platinum black serves as the electrode. This electrode obviously plays the part of an incompletely reversible oxygen electrode. After a preliminary cleaning of the electrode with emery paper it is placed in a 1% solution of chloroplatinic acid and platinized in the normal fashion for 15-20 seconds. If the platinization time is extended a thick layer of platinum black forms on the electrode and the potential on such an electrode is established only

very slowly. The electrode is finally washed with water, and then subjected to cathodic polarization for removal of adsorbed chloride by placing it in a 1 N ammonia solution. After 15-20 seconds the electrode is carefully washed, first with warm and then with cold water. The electrode can be used the day after platinization. It should be kept in water, where it remains sensitive for a long time.

A series of ferric chloride solutions of various concentrations (0.06-0.008 N) was prepared for investigation. They were standardized by duplicate gravimetric and volumetric determinations. A 0.1 N solution of sodium borate was used as the standard titrant.

Experimental Procedure. 0.25-2 ml of 0.06 N $FeCl_3$ solution diluted with 25 ml of water in a 200 ml beaker was titrated potentiometrically with 0.1 N borax in the presence of the indicator electrode. A saturated calomel electrode was used as the standard electrode. A galvanometer with a sensitivity of 10^{-7}A was used as the null instrument. The electrode potential during titration was established within 1-2 minutes after each addition of borax solution. The potential change of the electrode is determined on the one hand by a decrease in the hydrogen ion concentration of the solution during the titration of ferric chloride with borax, and on the other hand by the formation of the iron borates which only dissociate slightly. The change in $\Delta E/\Delta V$ during titration is shown in Fig. 5. Completely satisfactory results were obtained (Table 4).

The mean error of a determination for an iron concentration of the order of $2 \cdot 10^{-3}$ g is 0.1%. For lower concentrations of iron of the order of $3 \cdot 10^{-4}$ g the titration error amounts to 2%.

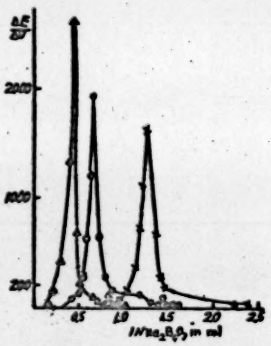


Fig. 5 Titration of 0.053 N $FeCl_3$ with 0.1 N $Na_2B_4O_7$. x = 2 ml; O = 1 ml; Δ = 0.5 ml.

Determination of Ferric Ions in the Presence of Acids

By means of the method proposed ferric ions can be determined not only in neutral solution, but also in acid solution. In this case two potential jumps are observed: the first-a small one-indicates the end of the titration of the free acid and the second- a large one-the end of the titration of the sum of the acid and ferric ions (Fig. 6, Curve 1). The small value of the first jump on the titration curve can be explained by the fact that the drop of borax added in excess after the first equivalence point has little effect on the electrode potential, since the iron borate which is formed only dissociates very slightly. Naturally in order to get a more marked potential jump during the titration of the acid in solution it is essential that the ferric ions should be bound in a more stable complex than ferric tetraborate.

$C_2O_4^{2-}$ ions are the most suitable for this purpose since they form a complex $[Fe(C_2O_4)_3]^{3-}$ with iron, the instability constant of this complex being $1.2 \cdot 10^{-24}$ [9] (Fig. 6, Curve II).

Experimental Technique. To a known volume of a mixture of a ferric salt and acid is added 1.5-2 g of dry sodium oxalate. The mixture is shaken up and diluted to 50 ml with water, after which it is titrated with 0.1 N borax potentiometrically (the free acid in solution is also determined by this method).

TABLE 4

Fe taken, g·10³	Fe found, g·10³	Interval drop, in mV	Error, g·10³
2.376	2.378	602-538	+0.002
1.188	1.188	613-525	–
0.594	0.594	614-493	–
0.336	0.339	580-465	-0.007

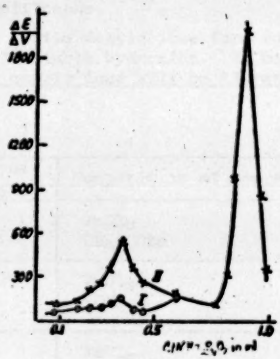


Fig. 6 Titration of free acid in a mixture of 1 ml 0.0343 N $FeCl_3$. Curve 1) without $Na_2C_2O_4$. Curve 2) with $Na_2C_2O_4$.

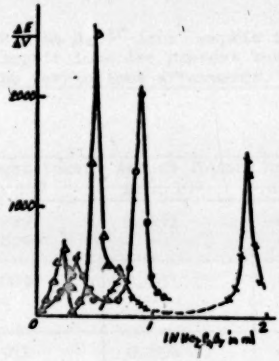


Fig. 7 Titration of 0.057 $FeCl_3$ in an acid medium. × – 2 ml; ○ – 1 ml; △ – 0.5 ml

A similar volume of the mixture (i.e. the original volume before dilution to 50 ml) is diluted to 25 ml with water and potentiometrically titrated against 0.1 N borax for the total hydrogen ions and ferric ions. The amount of iron is found by difference.

The concentration of the free acid in solution can also be determined by titration against 0.1 N NaOH in the presence of the same amount of sodium oxalate and with phenolphthalein as indicator.

The results are given in Table 5 and Fig. 7.

TABLE 5

Amount taken, in g·10³		Amount found, in g·10³		Error, in g·10³
HCl	Fe^{3+}	HCl	Fe^{3+}	
2.657	2.048	2.664	2.037	-0.011
1.328	2.024	1.332	1.019	-0.005
0.664	0.512	0.664	0.510	-0.002
0.332	0.256	0.333	0.254	-0.002
1.328	0.256	1.334	0.254	-0.002

Determination of Ferric Ions in the Presence of Other Ions

1. By means of the method described it is possible to determine iron in solutions of various complex compounds. The nature of many complex compounds in solution and their instability constants have been studied by Babko [10-14]. We have studied the potentiometric determination of iron by tetraborate in solutions of:

acetates, salicylates, thiocyanates, and fluorides. For this purpose known amounts of sodium acetate, salicylate, and fluoride, respectively, and potassium thiocyanate sufficient for the formation of the respective complex iron salts were added beforehand to a known amount of ferric salt solution. The complex compounds formed were then potentiometrically titrated with 0.1 N borax, as described previously.

Results of these determinations are given in Table 6.

2. The determination of iron in the presence of copper is of practical significance.

While ferric ions form soluble compounds with $B_4O_7^{2-}$ ions, cupric ions give an insoluble hydroxide. If both ferric and cupric ions are present together then the cupric ions will be titrated first and the ferric ions afterwards.

TABLE 6

No. of Expt.	Composition of the mixture	Amount taken in $g \cdot 10^3$	Amount found in $g \cdot 10^3$	Error in $g \cdot 10^3$
1	$FeCl_3$ CH_3COONa	1.229 328.0	1.231 -	+0.002 -
2	$FeCl_3$ KCNS	1.229 5.4	1.231 -	+0.002 -
3	$FeCl_3$ SalNa	0.912 19.2	0.894 -	-0.018 -
4	$FeCl_3$ NaF	1.08 8.4	1.08 -	- -
5	$FeCl_3$ $CuSO_4$	1.08 33.6	1.08 -	- -
6	$FeCl_3$ $CuSO_4$	1.974 2.924	1.974 2.861	- -0.063
7	$FeCl_3$ $CuSO_4$ HCl $Na_2C_2O_4$	1.862 2.924 2.430 2000.0	- - 2.419 -	- - -0.011 -
8	$FeCl_3$ $CuSO_4$ HCl	1.862 2.924 2.43	1.862 2.980 -	- -0.056 -
9	$FeCl_2$ $NiCl_2$, $CoSO_4$ Na_2WO_4 $(NH_4)_2MoO_4$ NH_4VO_3 SalNa	1.045 0.1 0.1 N 200.0	1.036	-0.009
10	$FeCl_3$ $NiCl_2$, $CoSO_4$, Na_2WO_4, $(NH_4)_2MoO_4$, NH_4VI_3, KCl, SalNa	1.045 2.430 200.0	0.070	+0.035

When copper ions are titrated in neutral media (Fig. 8), an increase in the potential jump is observed with decreasing salt concentration.

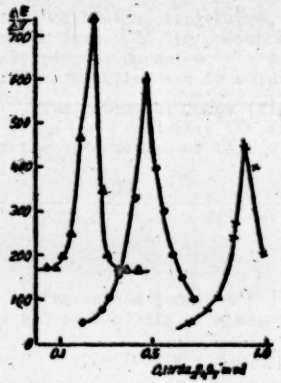


Fig. 8 Titration of 0.046 N $CuSO_4$ with 0.1 N $Na_2B_4O_7$
x - 2 ml; O - 1 ml; Δ - 0.5 ml.

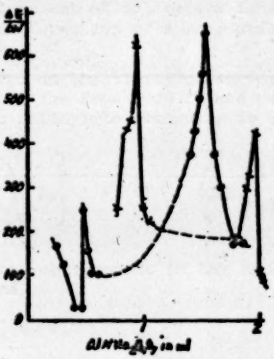


Fig. 9 Titration of 0.046 N $CuSO_4$ and 0.033 N $FeCl_3$ together with 0.1 N $Na_2B_4O_7$
x - 2 ml $FeCl_3$+2 ml $CuSO_4$
O - 2 ml $FeCl_3$+1 ml $CuSO_4$.

During the titration of ferric and cupric ions when present together two potential jumps are observed on the titration curve; the first indicates the end of the titration for cupric ions and the second indicates the end of the titration for the sum of cupric and ferric ions. The amount of iron is thus found by difference. It should be noted that as the amount of copper decreases and the amount of iron increases the first potential jump decreases, while the second, the sum of the two, increases (Fig. 9).

For the determination of ferric iron and copper in acid media the concentration of the free acid in solution must be preliminarily determined by an independent titration in the presence of oxalate ions as shown above.

In the second titration the concentrations of acid, cupric and ferric ions are all determined simultaneously. In this case the first potential jump on the titration curve corresponds to the end of the titration for the sum of acid and copper. The difference between this volume of borax and that used for neutralization of the acid (first titration) gives the amount of copper. The second potential jump on the titration curve corresponds to the total acid, ferric and cupric ions. The amount of iron is found by difference.

Results are given in Table 6.

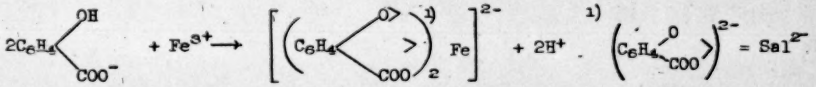
3. The determination of ferric iron in the presence of soluble salts of nickel, cobalt, vanadium, molybdenum, and tungsten is of great interest.

During the titration of such a system with borax, the nickel and cobalt ions behave similarily to the cupric ions and separate out as basic salts and hydroxides

and mask the fundamental iron titration. On addition to such a solution of some salicylate ions which form a stable complex with iron, the iron complex is first titrated with borax. To a solution of the mixture containing 1-2 ml of 0.05-0.06 N $FeCl_3$ and 0.1 ml each of approximately 0.1 N solutions of nickel, cobalt, molybdenum, vanadium and tungsten respectively, 0.2-0.3 g of sodium salicylate is added and the whole diluted to 50 ml with water prior to potentiometric titration with 0.1 N borax.

Molybdates, tungstates, and vanadates form slightly soluble compounds with ferric ions. In the presence of a sufficient amount of salicylate ions these precipitates do not settle out, because of the formation of a very stable complex of ferric salicylate in solution ($K = 4 \cdot 10^{-7}$).

Two potential jumps (Fig. 10) are observed on the titration curve; the first – a large one – indicates the end of the titration for free acid formed as the result of the interaction of ferric ions with sodium salicylate according to the equation:



The second jump, which is not so pronounced, corresponds to the formation in all probability of a mixed complex compound.

$$FeSal_2 + B_4O_7^{2-} \rightleftharpoons [FeSalB_4O_7] + Sal^{2-} .$$

The iron content is calculated from the first potential jump (Fig. 10). In this way iron can be determined not only in neutral mixtures but in solutions containing hydrochloric acid.

The experimental results obtained, which are completely satisfactory, are shown in Table 6.

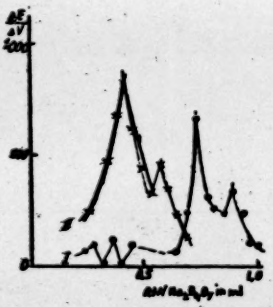


Fig. 10. Titration of 0.053 $FeCl_3$ with 0.1 N borax in the presence of other ions. II) In neutral media; I) in acid media.

Determination of Iron in Ores and Other Materials

The potentiometric method described above for the determination of ferric ions can be successfully applied to the determination of iron in various materials containing it, such as ores, coal, dolomite, etc.. In these cases 0.03-0.04 g of the well-ground substance is calcined for 10 minutes with ten times its weight of anhydrous sodium carbonate until a homogenous mass is obtained. The melt is worked up with 2-3 ml of concentrated hydrochloric acid until the whole goes into solution. (disappearance of black specks). The solution is then cooled and diluted with water to 100 ml in a standard flask. Free acid is determined in one aliquot as follows; to 10 ml of solution, 1 g of $Na_2C_2O_4$ is added. the solution diluted to 50 ml with water and titrated with 0.1 N alkali using phenolphthalein as indicator. In the second aliquot total acid plus iron is determined potentiometrically with 0.1 N borax.

The iron is calculated by difference.

The iron was determined in the same materials by another method, the iodometric method, as a check. Results are given in Table 7.

TABLE 7

Test material	Wt., in g[1]	Found		
		potentiometrically		iodometrically
		in g	in %	in %
Hornstone magnetite-aegirite	0.0294	0.01075	36.55	36.48
Hornstone schistous	0.0438	0.0207	47.30	47.25
Martite ore	0.0320	0.0238	74.62	74.60
Stone coal, Sample 1	0.0494	0.01758	35.40	35.25
Stone coal, Sample 2	0.1810	0.0152	8.40	8.25
Brown coal	0.6046	0.021	3.46	3.32
Lignite	0.0480	0.0030	6.3	6.3
Dolomite	0.3094	0.0028	0.905	0.89
Limestone	1.0010	0.00011	0.011	0.009
Kaolin	0.478	0.00153	0.320	0.28

[1] The weight of ash is given for the coal.

This method was also used by us successfully for the determination of iron in blood, medicinal preparations, and water.

SUMMARY

1. As a result of physico-chemical research it was established that ferric ions interact with tetraborate ions in solution to form a number of new complex iron borates.

2. On this basis a direct method for macro and micro potentiometric determinations of ferric iron both in neutral and acid media has been developed.

3. By this method iron can be determined in the presence of copper, nickel, cobalt, vanadates, molybdates, tungstates, etc.

4. This method can be used for the determination of iron in ores and other materials containing it.

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NEW VOLUMETRIC AND GRAVIMETRIC METHODS FOR THE DETERMINATION OF CADMIUM

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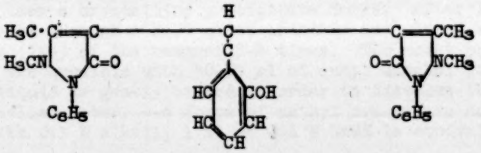
For the determination of cadmium in the presence of copper the poisonous and not always readily available potassium cyanide or brucine [1,2,3] are used. It has been shown recently that cadmium can be detected qualitatively by pyramidon in the presence of potassium iodide, and quantitatively by the antipyrine-bromide reagent [4] and by diantipyrylmethane. Hitherto very few methods have been described in the literature for the volumetric determination of cadmium; thus there is a reference to the possibility of titrating cadmium sulfide with iodine in acid solution; this method however does not give positive results because cadmium sulfide is contaminated with adsorbed salt [5]; Berg and Wurm precipitated cadmium with β-naphthoquinoline in the presence of potassium iodide and the amount of iodine determined in the precipitate with potassium iodate [5]. The determination of cadmium with 8-hydroxyquinoline [6] is based on the bromometric titration of the oxine combined with the metal. As our investigations have shown, it is possible to determine cadmium quantitatively by means of diantipyrylorthohydroxyphenylmethane:



or $C_{21}H_{28}O_3N_4$ (Mol.wt. 480.55). Diantipyrylorthohydroxyphenylmethane exists in the form of long white needles which are soluble to the extent of 0.1% in water and 5.5% in alcohol[1]. In acid media cadmium forms a slightly soluble complex of the composition: $(C_{28}H_{28}O_3N_4)_2H_2[CdBr_4]$ with diantipyrylorthohydroxyphenylmethane in the presence of potassium bromide.

The reaction proceeds as follows:

$$2D + 4Br^- + 2H^+ + Cd^{2+} = (D)_2H_2[CdBr_4]$$

(from here onwards diantipyrylorthohydroxyphenylmethane will be denoted by D). Cations of zinc, copper, cobalt, iron, aluminum, chromium and also of the alkali and alkaline earth elements do not form precipitates with D in the presence of bromine ions and consequently do not interfere with the determination of cadmium. Analysis of the crystalline precipitate formed during the determination of cadmium after recrystallization from aqueous alcohol and drying at 120° gave the following results: 0.2 g substance, AgBr 0.1144 g, $CdSO_4$ 0.031 g. Found Br 24.34%; Cd 8.35%.

For $[C_{28}H_{28}O_3N_4]_2H_2[CdBr_4]$ mol.wt. = 1395.18. Br calculated 22.91% and Cd 8.06%.

The volumetric method for the determination of cadmium is based on the action of alkali on the precipitate of $(D)_2H_2[CdBr_4]$, during which neutralization of

1) See reference H. Amal, Chem. Abs. 44, 6853 (1950).

TABLE 1

Property	$[C_{28}H_{28}O_3N_4]_2H_2[CdBr_4]$
Color	Pale rose
Solubility in water at 15°	0.06:100
" in alcohol	0.45:100
" in ether	insoluble
Behavior of a saturated aqueous solution of the compound with dilute H_2SO_4 and HNO_3	unchanged
Ditto towards conc. H_2SO_4 and HNO_3	unchanged
" " 1 N NaOH	$Cd(OH)_2$ precipitated
" " $AgNO_3$	Pale yellow precipitate of AgBr formed
Behavior of dry solid on heating in a capillary	Melts at 193°, changes into a red liquid

hydrogen ions occurs. Determinations of cadmium were made initially on pure salts. The reagent is prepared as follows: 0.25 g of D is dissolved with slight heating in 25 ml ethyl alcohol and to the solution 25 ml of 1 N sulfuric acid and 25 ml of a 5% solution of potassium bromide added. Each 5 mg cadmium requires 20-25 ml of the reagent solution described for precipitation. At low concentrations of cadmium, supersaturated solutions are apparently formed, because in order to accelerate the formation of a precipitate it is necessary to stir the mixture with a glass rod. Turbidity develops either immediately or after some time and then a crystalline precipitate forms. After 1½ hours the precipitate is filtered through a No.4 glass crucible and washed with 10 ml of a dilute solution (1:4) of the reagent 3-4 times. The moist precipitate is then washed from the crucible with 30-35 ml of ethyl alcohol into a 300-350 ml flask. The liquid is gently heated in order to dissolve the precipitate, 150 ml of distilled water, 4-6 drops of methyl orange are added and the solution titrated with 0.1 N alkali, 1 ml of 0.1 N NaOH is equivalent to 5.62 mg cadmium.

Results are given in Table 2.

TABLE 2

Expt. No.	Vol. of $Cd(NO_3)_2$ solution	Amount of cadmium, in mg	0.1 N NaOH used, in ml	Cadmium found, in mg	Absolute error, in mg
1	1	5	0.812	4.56	-0.44
2	2	10	1.81	10.17	+0.17
3	2	10	1.82	10.23	+0.23
4	3	15	2.6	14.61	-0.39
5	3	15	2.69	15.12	+0.12
6	4	20	3.6	20.23	+0.23
7	4	20	3.6	20.23	+0.23
8	5	25	4.31	24.22	-0.78
9	6	30	5.33	29.95	-0.05
10	6	30	5.36	30.12	+0.12

Determination of cadmium in the presence of copper is carried out as follows: to the solution containing a known weight of cadmium is added up to 0.5 g of cupric chloride - $CuCl_2 \cdot 2H_2O$, and then the reagent solution, 20-25 ml for each 5 mg of cadmium. The method then follows the procedure outlined above. Results of the determinations are given in Table 3.

TABLE 3

Vol. of $Cd(NO_3)_2$, in ml	Amount of cadmium, in mg	Amount of $CuCl_2 \cdot 2H_2O$ added, in g	0.1 N NaOH used, in ml	Cd found, in mg	Absolute error, in mg
3	15	0.5	2.65	14.89	−0.11
3	15	0.5	2.68	15.06	+0.06
4	20	0.5	3.4	19.11	−0.89
4	20	0.5	3.45	19.4	−0.6

The volumetric method given for determining Cd was used for the analysis of various alloys to which cadmium had been added. Two alloys were chosen for analysis: iron-aluminum bronze containing Cu, Fe, Al, Mn and Zn, and electron metal containing mainly magnesium, and also Al (7.7%) and Zn (1.65%). 1 g of the bronze was dissolved in 10 ml dilute (1:1) nitric acid and the solution obtained evaporated on a water bath, when 50 ml of water was added. 0.5 g of electron was dissolved in 10 ml hydrochloric acid (1:5) and 50 ml water. The solutions should be clear. The procedure adopted subsequently was that described above. Results are given in Table 4.

TABLE 4

Vol. of solution, in ml	Amount of $CdSO_4$ solution added, in ml	Cd content, in mg	0.1 N NaOH used, in ml	Cd found, in mg	Absolute error, in mg
		Iron-Aluminum Bronze			
15	4	20	3.6	20.23	+0.23
20	5	25	4.52	25.4	+0.4
15	4	20	3.5	19.67	−0.33
		Electron metal			
25	4	20	3.55	19.95	−0.05
25	5	25	4.55	25.01	+0.01

These results show that Mg, Al, Zn, Fe and Cu do not interfere with the volumetric determination of cadmium and that despite the fact that the amounts of these elements are greatly in excess of that of cadmium, the relative experimental error varies within ±3%. For the gravimetric determination of cadmium the precipitate is filtered through a No.4 glass crucible, washed with dilute reagent solution first and then with a mixture of alcohol and ether (1:7), and dried at 110-120° to constant weight. The conversion factor to cadmium is 0.08057. Results are given in Table 5.

Cadmium can be determined in the presence of copper also gravimetrically. Results are given in Table 6.

Cadmium can be precipitated with D at higher concentrations of D, sulfuric acid and potassium bromide; e.g., the precipitating reagent can be prepared as follows: 0.5 g of D is dissolved in 50 ml 50% alcohol to which are added 25 ml of 2 N sulfuric acid and 25 ml 10% potassium bromide. The drawback of such a solution is that after 4-5 hours it deposits a precipitate; it is necessary therefore to precipitate cadmium with a warm solution of the precipitant and not to leave the precipitate for more than 1½ hours.

If these conditions are observed and the method above followed for the determination of cadmium, good results are obtained (Table 7).

TABLE 5

$Cd(NO_3)_2$ taken, in mg	Cd content, in mg	Wt of ppt., in g	Cd found, in mg	Absolute error, in mg
1	5	0.0626	5.04	+0.04
2	10	0.1272	10.25	+0.25
3	15	0.1910	15.39	+0.39
1	5	0.0640	5.16	+0.16
2	10	0.1286	10.36	+0.36
3	15	0.1906	15.36	+0.93

TABLE 6

$Cd(NO_3)_2$ taken, in mg	Cd content, in mg	$CuCl_2 \cdot 2H_2O$ added, in g	Wt. of ppt., in g	Cd found, in mg	Absolute error, in mg
1	5	1	0.0630	5.077	+0.077
2	10	1	0.1264	10.18	+0.18
3	15	1	0.1924	15.5	+0.5
3	15	0.5	0.1782	14.36	-0.64

TABLE 7

Vol. of $CdSO_4$, in ml	Amount of Cd, in mg	Wt. of ppt., in mg	Cd found, in mg	Absolute error, in mg
1	5	0.0616	4.96	-0.04
2	10	0.1214	9.78	-0.22
2	10	0.1234	9.94	-0.06
2.5	12.5	0.1536	12.38	-0.12
3	15	0.1850	14.91	-0.09
1.5	7.5	0.0954	7.69	+0.19
2.5	12.5	0.1568	12.64	+0.14
3	15	0.1896	15.28	+0.28

Cadmium was successfully determined gravimetrically in different alloys to which it had been added. In addition to the volumetric and gravimetric methods for the determination of cadmium, attempts were made to develop a colorimetric method by diazotization of the reaction product, but in view of the low sensitivity of the color obtained the method is of no significance.

SUMMARY

A new complex compound has been prepared $[DH]_2[CdBr_4]$ and some of its properties studied.

New volumetric and gravimetric methods have been developed for the determination of cadmium in the presence of magnesium, aluminum, zinc, copper and other metals.

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DETERMINATION OF CUPROUS OXIDE, CUPRIC OXIDE, AND METALLIC COPPER IN COPPER POWDERS

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One of the most difficult problems to solve in analytical chemistry is that of the determination of copper in its different forms. Information in the literature is very scanty.

Various methods have been proposed by Tananaev [1], Lavrukhina [2], Hard and Clerk [3] and other investigators for the extraction and determination of metallic copper and cuprous oxide in mixtures of Cu, Cu_2O, CuO. Of these methods Lavrukhina's method [2] gives the most satisfactory results.

Our problem was to work out an accurate method for the determination of cuprous oxide, cupric oxide, and metallic copper in copper powders. The copper powders which served as the object of our investigation and which were prepared by an electrolytic method are used to a considerable extent at present for the production of so-called self-lubricating bronze bearings. These bearings are produced by a metallo-ceramic process and have a composition similar to that of cast bronze bearings: they usually contain about 90% copper; 10% tin, and sometimes 1.5-4.5% graphite.

The industry which produces these self-lubricating bearings lays down certain specifications for the chemical composition of the copper powders. In the production of these powders therefore it is essential to be able to determine rapidly the metallic copper content and that of certain oxygen compounds of copper, viz., cupric and cuprous oxides. Up to the present, however, the possibility of carrying out such determinations has been small as far as information in the literature is concerned.

Method, Reagents, and Materials

N.A.Tananaev's investigations [1] were used as the basis for the method. Ammonium chloride solution was used for the quantitative separation of cuprous oxide from cupric oxide and the metallic copper, while a dilute solution of sulfuric acid was used for the separation of cupric oxide from metallic copper. The metallic copper is dissolved in nitric acid. After separation of the mixture into its components the copper is determined by iodometric, electogravimetric, and permanganate methods.

The results in Table 1 show that metallic copper is practically insoluble in ammonium chloride and only an insignificant amount of cupric oxide is dissolved. The cupric copper which does go into solution forms a complex ion, the reaction of which with metallic copper is considerably weakened. If the reaction is carried out in an atmosphere of CO_2 and oxygen-free solutions are used the cuprous oxide is not oxidized to the bivalent state and the metallic copper does not dissolve. The cupric copper which goes into solution does not interfere with the determination

TABLE 1

Solubility of Copper Compounds in 15% Ammonium Chloride Solution. An aliquot is treated with ammonium chloride for 5 minutes while heating to 100° in a stream of CO_2. The amount of copper which enters solution is determined iodometrically.

Experiment No.	Weight of sample, in g			Amount of NH_4Cl, in ml	Amount of the copper compound which goes into solution
	Metallic	Cuprous	Cupric		
1	0.1000	–	–	15	0.0000
2	0.1000	–	–	15	0.0000
3	–	–	0.1000	15	0.0002
4	–	–	0.1000	15	0.0002
5	–	0.1000	–	15	0.0999
6	–	0.1000	–	15	0.0999

of the cuprous oxide, particularly in the permanganate method. Dilute sulfuric acid readily dissolves cupric oxide, partially dissolves cuproud oxide, but does not dissolve metallic copper to any extent.

Preliminary Investigations

Initially experiments were carried out on metallic copper with each of the oxides in turn. Afterwards metallic copper was determined together with one of the oxides in the presence of the other oxide (only one of the components was determined in the mixture, assuming the presence of the other but not quantitatively evaluating it). Finally all the components were determined in the mixture of cupric and cuprous oxides and metallic copper.

Cuprous oxide was determined as follows. A sample was treated with 1 N ammonium chloride. In order to accelerate the rate of solution the solution was heated almost up to the boil. The solution obtained of the complex compound of univalent copper was diluted with water, acidified with sulfuric acid and titrated with 0.1 N potassium permanganate[1]. Potassium iodide was thenadded to the solution and the iodine liberated titrated with 0.1 N sodium thiosulfate[2] using starch as an indicator. In this way the cuprous oxide is first determined by permanganate and then by a iodometric method.

From this it appears that 1) cuprous oxide dissolves only very slowly in 1 N ammonium chloride, and 2) the permanganate method gives much lower results than the iodometric one, which gives the correct results. On the basis of systematic analysis it was established that in order to increase the rate of solution it is better to use an ammonium chloride solution with a concentration of not less than 15%.

In order to prevent oxidation of the univalent copper by aerial oxygen which can affect the results considerably, the cuprous oxide should be dissolved, and all further operations conducted in an atmosphere of CO_2, using solutions from which all the air has been expelled by prolonged bubbling of CO_2 through the solutions.

Cuprous oxide is thus determined in the presence of metallic copper and cupric oxide. The solution of cuprous oxide in ammonium chloride is filtered from the cupric oxide and metallic copper and the copper in solution determined by the permanganate and iodometric methods. Results are given in Table 2.

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1) Initially the titration with permanganate was carried out after addition of a solution of ferric chloride [3], but this practice was discontinued since addition of $FeCl_3$ proved to be unecessary.

2) Excess permanganate is removed by addition of one or two drops of sodium oxalate.

Cupric oxide is determined iodometrically after dissolving the cupric oxide in sulfuric acid, by titration with 0.1 N sodium thiosulfate. In those cases where the cupric oxide is mixed with metallic copper and cuprous oxide, the latter is preliminarily removed by ammonium chloride solution. The residue, consisting of cupric oxide and metallic copper, is then worked up with dilute sulfuric acid. The solution obtained is diluted with water, filtered from metallic copper, and the copper in solution determined iodometrically or by the method of internal electrolysis. Results are given in Table 3.

TABLE 2

Determination of copper as cuprous oxide by the permanganate and iodometric methods

The sample is dissolved in 15% ammonium chloride. Sulfuric acid is added to the solution thus obtained, and the copper is determined by the permanganate method and then by the iodometric method

Experiment No.	Weight of cuprous oxide sample, in g	Vol. of 0.1254 N $KMnO_4$ used, in ml	Vol. of 0.0963 N $Na_2S_2O_3$ used, ml	Amount of copper, g		Difference	
				Found	Actual	Absolute, in g	Relative, in %
1	0.1000	–	14.47	0.0886	0.0888	−0.0002	0.23[1]
2	0.1000	10.10	–	0.0805	0.0888	−0.0083	9.35
		–	14.50	0.0888	0.0888	−0.0000	0.00
3	0.1000	9.00	–	0.0717	0.0888	−0.0171	19.23[2]
		–	14.35	0.0878	0.0888	−0.0010	1.01
4	0.1000	10.40	–	0.0829	0.0888	−0.0059	6.74[3]
		–	14.50	0.0888	0.0888	−0.0000	0.00
5	0.1000	10.50	–	0.0837	0.0888	−0.0051	5.77[3]
		–	14.37	0.0879	0.0888	−0.0009	1.04
6	0.1000	9.10	–	0.0725	0.0888	−0.0163	18.35[4]
		–	14.40	0.0881	0.0888	−0.0007	0.79

1) Sample dissolved with warming in 15% ammonium chloride without CO_2.
2) Sample dissolved in the cold without CO_2.
3) Solution and titration of the cuprous oxide carried out in CO_2.
4) Sample dissolved in the absence of CO_2. Before titration a solution of ferric chloride was added.

TABLE 3

Determination of copper as cupric oxide by electrolytic and iodometric methods. The sample of cupric oxide is dissolved in sulfuric acid (1:3), and the copper in solution determined electrolytically and iodometrically.

Expt. No.	Weight of cupric oxide sample, g	Vol. of 0.0963 N $Na_2S_2O_3$ used, ml	Amount of copper, in g		Difference		Observation
			Found	Actual	Absolute, g	Relative, %	
1	0.1000	13.02	0.0797	0.0799	−0.0002	0.24	Cuprous oxide removed with 15% ammonium chloride and metallic copper filtered off after dissolving cupric oxide in H_2SO_4
2	0.1000	13.08	0.0798	0.0799	−0.0001	0.15	
3	0.1000[1]	13.00	0.0796	0.0799	−0.0003	0.40	
4	0.1000[1]	13.05	0.0799	0.0799	−0.0000	0.00	
5	0.1000[1]	13.08	0.0800	0.0799	+0.0001	0.11	

1) The cupric oxide samples contain 0.1 g each of cuprous oxide and metallic copper as well as cupric oxide.

Metallic copper was determined iodometrically after dissolving it in acid. The sample of pure copper was dissolved in nitric acid (1:1) or in concentrated sulfuric acid with heating. When metallic copper is mixed with cuprous and cupric oxides, the cuprous oxide is first removed by dissolving it out with ammonium chloride, then the cupric oxide is removed with dilute sulfuric acid and the metallic copper left determined by the method described above.

Since it is necessary to filter twice and the presence of the filter interferes with the determination of the end point of the titration during iodometric titration, the last filter with its precipitate is dried and ignited in a porcelain crucible. Results are given in Table 4.

When it is necessary to determine all three components in the mixture the procedure is as follows: The cuprous oxide is removed by dissolving it out with ammonium chloride, the residue is extracted with dilute sulfuric acid to remove the cupric oxide, while the metallic copper which remains is dissolved in concentrated nitric or sulfuric acids. The copper is then determined iodometrically in all three solutions, in addition the cuprous oxide is determined by the permanganate method.

TABLE 4

Determination of Copper in Metallic Copper Electrolytically and Iodometrically.

The sample of electrolytic copper is dissolved in nitric acid; the solution is evaporated to dryness; the residue is dissolved in sulfuric acid and the solution formed diluted with water. The copper is determined electrolytically and iodometrically.

No. of expt.	Amount of sample of metallic copper, in g	Vol. of 0.0963 N $Na_2S_2O_3$ used, in ml	Amount of copper in, g		Difference		Observation
			Found exptl.	Actual	Absol.	Relative (%)	
1	0.1000	16.35	0.1001	0.1000	+0.0001	0.10	Cuprous oxide removed with ammonium chloride and cupric oxide with sulfuric acid
2	0.1000	16.33	0.1000	0.1000	0.0000	0.00	
3	0.1000[1]	16.45	0.1007	0.1000	+0.0007	0.70	
4	0.1000[1]	16.25	0.0995	0.1000	-0.0005	0.50	

[1] The samples of metallic copper contain 0.1 g of cuprous and cupric oxides.

In the titration of copper with permanganate a standard solution of manganese sulfate is added to counteract the interference of the Cl^- ions. The normality of the permanganate solution was determined with sodium oxalate in the presence of ammonium chloride.

As a result of these preliminary tests the folowing analytical procedure was worked out for the analysis of mixtures of cuprous oxide, cupric oxide and metallic copper.

The test mixture, which contained 0.1 g each of metallic copper, cuprous oxide and cupric oxide, was weighed out into a 100-200 ml dry conical flask and all the air expelled by passing CO_2. 10-15 ml of 15% ammonium chloride solution is added. The solution is heated until all the cuprous oxide is dissolved, 2-3 minutes are usually enough (until all the red particles disappear). The solution is then filtered in a stream of CO_2, the solution diluted to 40 ml with water, and 10-15 ml of 1 N sulfuric acid added. The cold solution is then titrated with potassium permaganate until a faint rose color is obtained, which persists for 2 minutes. A blank is performed at the same time.

The excess permanganate is reduced with a solution of sodium oxalate. 2-3 g of potassium iodide is added to the colorless solution and the iodine liberated is titrated with 0.1 N sodium thiosulfate, using starch as an indicator. From the amount of potassium permanganate and sodium thiosulfate used the amount of cuprous oxide can be calculated from the formula:

$$P_{Cu} = K \cdot V \cdot 0.06354, \qquad (1)$$

where P_{Cu} is the amount of copper as cuprous oxide; K is the normality of the solution; V is the volume of the titrant; and 0.06354 is the milliequivalent of copper.

The filter and residue of metallic copper and cupric oxide are transferred to a 50-100 ml conical flask and worked up with 10-15 ml of dilute sulfuric acid (1:3). The solution of cupric sulfate formed is filtered and the filter washed 3-4 times with water, the filtrate then being diluted to 50 ml and the copper determined iodometrically. The amount of cupric oxide can be calculated from Formula (1).

TABLE 5

Determination of copper in a mixture of cuprous oxide, cupric oxide, and metallic copper

The sample, which consists of cuprous oxide, cupric oxide, and metallic copper, is treated successively with 15% ammonium chloride solution with heating in a stream of CO_2, dilute sulfuric acid (1:3), and nitric acid (1:1). The solutions obtained are analyzed separately for their copper contents.

Expt. No.	Amount of copper sample, in g			Vol. of 0.1254 N $KMnO_4$ used, ml	Vol. of 0.0963 N $Na_2S_2O_3$ used, ml	Amount of copper, in g		Difference	
	Metallic	Cupric	Cuprous			Found	Actual	Absolute (g)	Relative %
1	0.1000	–	–	–	16.21	0.0992	0.1000	−0.0008	0.80
	–	0.1000	–	–	13.05	0.0799	0.0799	0.0000	0.00
	–	–	0.1000	10.80	–	0.0862	0.0888	−0.0026	2.96
	–	–	–		14.60	0.0900	0.0888	+0.0012	1.35
2	0.1000	–	–	–	16.20	0.0992	0.1000	−0.0008	0.80
	–	0.1000	–	–	12.75	0.0788	0.0799	−0.0011	1.37
	–	–	0.1000	10.90	–	0.0869	0.0888	−0.0019	2.16
					14.50	0.0888	0.0888	0.0000	0.00
3	0.1000	–	–	–	–	–	–	–	–
	–	0.1000	–	–	12.80	0.0784	0.0799	−0.0015	1.93
	–		0.1000	11.00	–	0.0877	0.0888	−0.0011	1.15
			–	–	14.05	0.0888	0.0888	0.0000	0.00
4	0.1000	–	–	–	15.75	0.0904	0.1000	−0.0036	3.54
	–		0.1000	9.8	–	0.0781	0.0888	−0.0107	12.10
				–	14.50	0.0888	0.0888	0.0000	0.00

The residue of metallic copper and the filter itself are removed to a porcelain crucible in which they are dried, ignited, and calcined. The calcined residue is finally dissolved in sulfuric acid. The copper is determined iodometrically. The results given in Table 5 show that our method gives satisfactory results. The difference between individual determinations lies within the limits of the permissible error.

Determination of Copper in Copper Powders

The method described above was used for the analysis of copper powders, the results for which are given in Table 6. In order to compare the results obtained by the method described and those obtained by other methods, a series of determinations of the copper oxides and metallic copper was carried out using Lavrukhina's method [2]. Results by the different methods are compared in Table 7. Table 7 shows that results by Lavrukhina's method are in good agreement with those obtained by our method.

SUMMARY

1. A rapid method has been worked out for the determination of cupric oxide, cuprous oxide, and metallic copper in mechanical mixtures of all three.

2. Cuprous oxide can be determined with an accuracy up to 1% by the iodometric method and up to 2-3% by the permanganate method. The cupric oxide and metallic copper can be determined with an accuracy of up to 1% (relative).

TABLE 6

Determination of cuprous oxide, cupric oxide and metallic copper in copper powders. The determinations were carried out by the method described

No. of expt.	Amount of copper powder, in g	Copper found, in g			Observation
		Metallic	Cuprous	Cupric	
1	0.5000	0.3220	0.0010	0.1780	The cupric and cuprous oxides are calculated as cupric and cuprous respectively.
	0.5000	0.3200	0.0010	0.1720	
2	0.5000	0.3330	0.0040	0.1630	
	0.5000	0.3300	0.0040	0.1600	
3	0.5000	0.3500	0.0020	0.1420	
	0.5000	0.3450	0.0020	0.1420	
4	0.5000	0.3900	0.0010	0.1000	
	0.5000	0.3900	0.0010	0.1000	
5	0.2000	0.1700	0.0020	0.0290	
	0.2000	0.1700	0.0010	0.0300	
6	0.5000	0.4840	–	0.0050	
	0.5000	–	–	–	

TABLE 7

Comparison of results of copper powders obtained by our method and Lavrukhina's method.

No. of expt.	Designation of sample	Wt. of sample, in g	Copper found, in g (Lavrukhina's method)			Copper found, in g (Our method)		
			Metallic	Cuprous	Cupric	Metallic	Cuprous	Cupric
1	Copper powder No. 1	0.5000	0.3220	0.0010	0.1780	0.3200	0.0010	0.1780
2	Copper powder No. 2	0.5000	0.3330	0.0040	0.1630	0.3320	0.0030	0.1630
3	Copper powder No. 3	0.5000	0.3420	0.0020	0.1400	0.3500	0.0020	0.1420
4	Copper powder No. 4	0.5000	0.3820	0.0030	0.1000	0.3900	Traces	0.0900
5	Copper powder No. 5	0.2000	0.1600	0.0010	0.0300	0.1700	0.0015	0.0290
6	Copper powder No. 6	0.3000	0.2700	Traces	0.0380	0.2600	Traces	0.0380

3. Determination of cuprous oxide, cupric oxide and metallic copper can all be done on one sample.

4. One hour is sufficient for a complete analysis.

5. The main advantage of the method is its simplicity.

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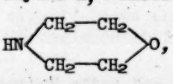
THE USE OF MORPHOLINE IN ANALYTICAL CHEMISTRY

M.V.Rodina

Ural Pedagogical Institute

Morpholine C_4H_9NO, or tetrahydro-1,4-oxazine



is a colorless, oily, volatile liquid which has a characteristic amine odor. It dissolves readily in water, alcohol and ether; its melting point is 128.9°; its hardening point 4.9; its specific gravity 0.99; it burns with a bluish flame.

In its chemical properties morpholine is a weaker base than ammonia. It forms easily crystallizable salts with acids and precipitates many heavy metal salts from their aqueous solutions mainly as the hydrated oxides or basic salts.

There is practically no information of the use of morpholine in analytical chemistry in the literature.

We have shown the possibility of using morpholine in qualitative analysis as a reagent for the identification of bismuth and cadmium ions.

Detection of Bismuth with Morpholine in the Presence of Potassium Iodide

One of the characteristic reactions for bismuth is the formation of crystalline precipitates of complex salts of a red, yellow or orange color on the addition of potassium iodide and organic bases. We studied this reaction using morpholine as the base and found that morpholine gives an orange-red precipitate with bismuth salts in the presence of potassium iodide in a nitric acid solution. Under the microscope the crystals appear as rhombs, tetragons and hexagons. The precipitate is insoluble in alcohol, soluble in hydrochloric acid and excess potassium iodide, but decomposes on treating with water or alkalis.

It was observed that on addition of 10% potassium iodide solution dropwise to a nitric acidified solution of a bismuth salt containing morpholine in a test tube, the sensitivity of the reaction corresponds to a limiting concentration of bismuth of 1:4400.

The sensitivity of the reaction can be considerably increased if it is carried out as follows; 2-3 ml of bismuth nitrate is placed in a test tube and the morpholine added. A white precipitate of bismuth hydroxide is formed; at low concentrations the precipitate is practically imperceptible nevertheless the solution is filtered through a filter paper. The filter paper is then unfolded and a drop of nitric acid placed (1:10) on its center. This spot is touched with a capillary tube containing a 10% solution of potassium iodide. An orange red precipitate is formed. This method gives a clear cut result at a concentration of 1:50,000 of bismuth. At concentrations of 1:100,000 an indistinct reddish coloration is produced.

This reaction is very suitable for the detection of traces of bismuth in a solution containing large amounts of copper and cadmium while carrying out the normal systematic qualitative analysis (in the sub-group copper, bismuth, and cadmium).

Method of identification. Morpholine is added to the test solution until an alkaline reaction is obtained; at this point copper, cadmium, and bismuth are precipitated as hydroxides. To the solution ammonium nitrate is added. The precipitate of the hydroxides of copper and cadmium dissolves with the formation of ammoniates, while the bismuth hydroxide is filtered (even though at low concentrations of bismuth it seems to be clear), and the filter paper washed. The filter paper is then unfolded, moistened with morpholine, and a drop of nitric acid placed on the center; this point is touched with a capillary containing 10% potassium iodide. An orange-red color indicates the presence of bismuth.

A Microcrystalloscopic Reaction for Cadmium Based on the Formation of Cadmium Morpholinethiocyanate

The capacity of cadmium to give slightly soluble, complex salts with a characteristic crystalline form with organic bases and ammonium thiocyanate has found application in the microcrystalloscopic detection of cadmium. We studied this reaction using morpholine as the base.

It was observed that a few minutes after the addition of a solution of morpholine and potassium or ammonium thiocyanate to a solution of a cadmium salt, a coarse, colorless crystalline precipitate of cadmium morpholinethiocyanate is formed. The rate of formation depends on the concentration and can be increased by rubbing the sides of the test tube with a glass rod. This precipitate is soluble in excess ammonium thiocyanate (but not in excess potassium thiocyanate), and readily dissolves in acetic and mineral acids; on shaking up with a large volume of water it hydrolyzes with the formation of white flocs of cadmium hydroxide. The precipitate only settles out on long standing from very dilute solutions.

For microcrystalloscopic detection the procedure adopted is as follows. A drop of test solution is placed on a glass slide and a drop of 20-30% solution of morpholine added, together with a crystal of potassium thiocyanate. On standing, or on rubbing with a glass rod, a crystalline precipitate is formed, which is then examined under the microscope. Pure morpholine or concentrated solutions of it should not be used for the reaction, since morpholine forms a salt with potassiumthiocyanate, which on rubbing with a glass rod separates out as colorless crystals in the form of trapeziums, reactangles and hexagons, needles, etc. 20-30% morpholine does not form crystals with potassium thiocyante.

It was found that on addition of a crystal of potassium thiocyanate to a mixture of a drop of a solution of cadmium salt and a drop of 20-30% morpholine, colorless crystals of cadmium morpholinethiocyanate are formed as parallellograms, rhombs, and crystals of other characteristic shapes (Figs. 1, 2, and 3,– see Plate page 359). In moderately dilute solutions of cadmium salts, the precipitates which are formed by friction with a glass rod have a more characteristic form, although the crystals are smaller; in very dilute solutions, single characteristic crystals are formed after several minutes. The limit of identification is 0.1 μg of cadmium. The limiting concentration is 1:10,000. The sensitivity of this reaction is higher than that of similar reactions with other organic bases.

In addition to cadmium, zinc, lead, mercury and copper and moderately concentrated solutions of nickel give crystalline precipitates under the conditions indicated above. If both cadmium and copper are present, greenish-yellow crystals are formed, probably of the mixed salt.

The author wishes to express her thanks to I.P.Ryazanova for permission to carry out this work in the Saratov University laboratory, and to V.A.Voshchin for preparing the microphotographs of cadmium morpholinethiocyanate.

Received March 12,1951.

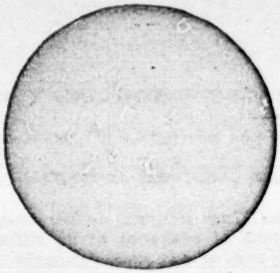


Fig. 1. Crystals of cadmium morpholine-thiocyanate from Cd^{2+} solutions of concentration 1:5000 (magnification 120).

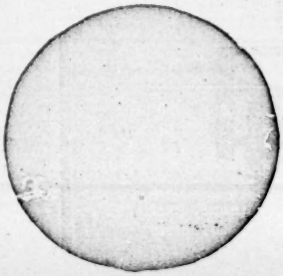


Fig. 2. Crystals of cadmium m morpholinethiocyanate from Cd^{2+} solutions of concentration 1:1000 (magnification 120).

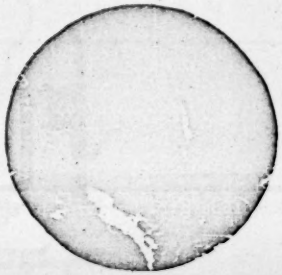


Fig. 3. Crystals of cadmium morpholinethiocyanate from Cd^{2+} solutions of concentration 1:200 (magnification 120).

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DETERMINATION OF SMALL AMOUNTS OF NITROGEN IN GASES

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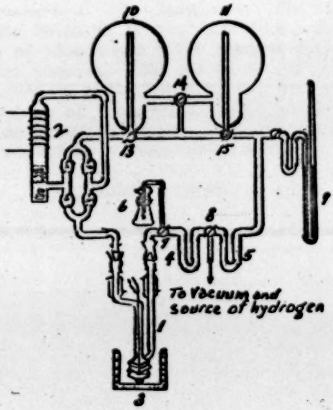
Hydrogen and other gases often contain small amounts of nitrogen. By means of the method described below it is possible to determine nitrogen directly in gaseous mixtures. In its simplest form the method can be applied to the determination of traces of nitrogen in hydrogen.

The hydrogen which contains nitrogen is circulated several times through a closed system containing a catalyst for converting the nitrogen into ammonia and a trap cooled with liquid air until all the nitrogen has been removed as ammonia. The amount of ammonia formed is then determined by the usual methods.



The apparatus is shown schematically in the diagram. The total volume of the apparatus as used in our experiments could be varied from 1-10 liters (the volume is changed by including or excluding supplementary flasks 10 and 11 by means of the taps 13, 14 and 15). The gas is circulated by means of a glass electromagnetic pump 2 [1]. Flask 1 made of pyrex contains 30 g of the catalyst for ammonia synthesis in the form of grains 2-3 mm in diameter. The catalyst is reduced at the

begining of an experiment. The vessel is provided with a coil for preliminary heating of the gas. The gas is heated by means of an electric furnace 3. The temperature of the catalyst is measured with a thermocouple. Experiments are conducted at 475°. Circulation of the gas mixture is continued until the ammonia which is frozen in the tube 4 filled with broken glass ceases to be formed. For a content of 1% of nitrogen in the test gas a few hours is necessary for complete conversion into ammonia at a circulating rate of 300-500 liters per hour. In order to check that all the nitrogen has been converted into ammonia, U tube 5 which precedes tube 4 is periodically cooled with liquid air. The absence of any deposit of solid ammonia in this tube indicates the end of the reaction. The trap 4 is then allowed to warm up to room temperature and the ammonia blown by a stream of hydrogen through tap 8 into flask 6 containing standard sulfuric acid. Excess acid is then backtitrated with NaOH using a microburet. Before intake of a new sample the apparatus is evacuated[1]. By means of this method nitrogen can be determined in hydrogen at a concentration of $1 \cdot 10^{-3}$% vol. with a possible error of $\pm 5 \cdot 10^{-5}$.

The method can also be used for the determination of small amounts of nitrogen in various gases such as argon or other inert gases[2]. A small amount of nitrogen-free hydrogen must be added to other gases containing nitrogen before carrying out the procedure described above.

The method can also be used for freeing hydrogen from contamination with nitrogen. Hydrogen cylinders usually contain up to 1% nitrogen. It could also be used for removing nitrogen from inert gases. E.g. if it is required to determine nitrogen in argon using hydrogen from a cylinder, the hydrogen is allowed into the system up to a pressure of 1/2 atmosphere. The nitrogen in the hydrogen is converted into ammonia which is frozen in trap 4. After disconnecting tap 4 from the system by means of taps 7 and 8 the ammonia is removed by pumping out in a frozen state under high vaccuum. The gas to be analyzed is then led into the system, the amount introduced being found by the increase in pressure measured by manometer 9 (the volume of the system should be known). The determination is then carried out as described above. The hydrogen used for combining with the nitrogen can be removed by heated cupric oxide.

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Received November 23, 1951

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1) Air must be excluded from the apparatus since this will lead to deterioration of the catalyst

2) I.P.Krichevsky pointed this out.

AN APPARATUS FOR THE DETERMINATION OF NITROGEN IN GASESOUS MIXTURES

I.G.Lesokhin, B.A.Kopylev and A.Ya.Averbukh[1)]

Leningrad Technological Institute,

Up to the present it has been current practice in gas analysis to assume that the gaseous residue which cannot be determined by the use of the normal absorbents or by fractional combustion, is nitrogen. This residue is determined at the end of the determination by difference. Such a method inevitably leads to a lower accuracy since all the errors in the individual determinations add up in the residue. In view of the fact that a direct determination of nitrogen is necessary for many investigations, various methods have been proposed during the last 50 years which to some extent answered the purpose for a particular problem.

Lidov [1] studied the absorption of nitrogen by metallic magnesium and mixtures of magnesium and calcium as far back as 1902 and on this basis proposed a method for the determination of nitrogen in its mixtures with other gases and in chemical compounds. His apparatus and technique have been simplified by Blumstein [2]. Henrich and Eichorn [3] described an apparatus in which the nitrogen is ignited by means of an electric discharge in the presence of hydrogen. Fisher and Ring [4] used calcium carbide for binding the nitrogen.

Dementeva [5] for the determination of nitrogen in gases recommended a special apparatus in which all the gases are ignited to CO_2 and H_2O. CO_2 is absorbed and the gas left is assumed to be nitrogen.

All the apparatuses described above however are of complicated construction and consequently they are expensive and are difficult to control.

In 1950-1951 we constructed a simpler and more portable apparatus than the rather cumbersome appartus which have been proposed previously and which are rarely used in practice.

Description of Apparatus

The apparatus consists of the following major parts (See diagram). A measuring buret of 5-10 ml capacity fitted with a three-way tap 1 and a levelling tube with a tap 3 are fixed on a glass frame provided with two leads (inlet and outlet for water to maintain the temperature constant during an analysis) and a thermometer.

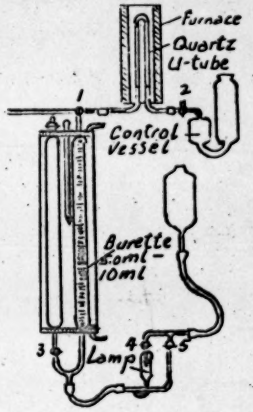
A pear-shaped vessel containing mercury is connected through a rubber tube with a lamp in the form of a cylinder. The additional tube with two taps 4 and 5 serves as a regulator for the velocity with which the gas is removed from the buret into U-tube. A control vessel with a three way tap 2 which acts as a receiver for excess gas not absorbed on passing through the U-tube. An electric furnace working at 800-900°. A quartz U-tube.

Preparation of the Apparatus for Analysis

Clean mercury is poured into the levelling pear shaped vessel, tap 5 is opened and the connecting rubber tube and all the glass connections filled, care

1) Student V.P.Bogdashev participated in this work.

being taken to exclude any bubbles of air. In this way all the measuring buret is filled with mercury. During this operation the buret is open to the atmosphere via tap 1. Taps 2, 3 and 4 are closed. When all the measuring buret is filled with mercury (right up to the zero mark) tap 5 is closed again.



The U-tube is then swept out with any inert gas or hydrogen which are free from any contaminations. The U-tube is a bent quartz tube (height 8-10 cm and internal diameter of 4-5 mm) filled with powdered metallic magnesium (2-3 g). The U-tube has an internal diameter of 5 mm and an external diameter of 7 mm. The bent back ends of the U-tube are made in the form of capillaries with external diameter 7 mm and internal diameters of 1 mm and 2 mm on different sides. The magnesium is sieved beforehand through a 40 mesh sieve (40 openings/cm^2) washed thoroughly with carbon tetrachloride and dried.

In order to fill the U-tube with magnesium in the least possible time in one operation we suggest the following procedure: the end of the U-tube connected to the smaller capillary is covered with a wad of cotton wool and pressed against a vaccuum lead, while the other end is placed in the box containing the metallic magnesium. By moving the end of the U-tube about continuously in the box containing the powder the U-tube can be filled in about 1-2 minutes.

Before a run it is essential to calcine the U-tube with hydrogen in a crucible or muffle furnace for one hour at 800° in order to remove any gases adsorbed by magnesium (mainly hydrogen). If argon is being used there is no need to calcine.

Although magnesium on its own absorbs nitrogen much slower than when it is mixed with calcium oxide and metallic sodium and considerably slower than metallic calcium on its own, nevertheless possible errors arising from the presence of hydrogen or methane etc. in the test gas are excluded.

Metallic calcium is known to absorb hydrogen actively forming calcium hydride, while if calcium oxide is used there is a possibility of a reaction between it and any hydrocarbons at the expense of the oxygen of the CaO.

Argon or hydrogen is passed through the leading-in capillary, tap 1, U-tube and through tap 2 open to the atmosphere. Tap 2 is then closed so that the U-tube is completely sealed off (tap 1 is also switched to exclude the atmosphere) and the control vessel opened to the atmosphere.

Analytical Procedure

After the apparatus has been prepared for analysis as described above, the test mixture of gases (residue after absorption of CO_2; C_nH_{2n}; O_2 and CO by the usual methods of gas analysis) is sucked through the inlet capillary and tap 1 (open to the atmosphere) into the measuring buret. In order to do this the levelling pear-shaped vessel is lowered and the gas intake regulated by means of tap 5. When the intake of gas for analysis is complete, tap 5 is closed, tap 3 is opened and the gas adjusted to normal pressure (by levelling with the pear shaped vessel until the levels in the measuring buret and the levelling tube coincide) and readings made of the exact volume of gas taken for analysis, the temperature, and the

barometric pressure. The electric furnace is then switched on and when the U-tube has been heated to the requisite temperature (while the U-tube is being heated it is connected via tap 2 with the control vessel for egress of the expanding hydrogen or argon) the test gas is allowed to pass through it.

The measuring buret is connected with the U-tube via tap 1, and on opening tap 2, tap 4 is also slowly closed so that the mercury, with the requisite velocity, gradually flows through the capillary branch. The mercury which flows out drives the gas from the measuring buret into the U-tube. The gas which passes through the heated metallic magnesium proceeds to the control vessel. In this case the operation of circulating the gas through the U-tube must be repeated, the gas being led back from the control vessel into the measuring buret (the flow rate of the gas is 2-3 ml/minute).

In order to carry out the recirculation tap 4 is closed and tap 5 is opened and with taps 1 and 2 also opened the pear-shaped vessel with the mercury lowered. When this is done the gas from the control vessel quickly passes through the U-tube into the measuring buret (because of the vaccuum created by the mercury flowing rapidly from the measuring buret, through tap 5 and the additional tube into the pear shaped bulb which has been lowered). The transfer is continued until the mercury from the control vessel is sealed off by the capillary at tap 2. The gas is repeatedly passed through the U-tube until the volume of the residual mixture remains a constant. The nitrogen content of the test mixture is then calculated from the difference in volume of gas before and after circulation through the system. The volume is measured after the U-tube has cooled. When this is done, part of the gas is transferred from the buret into the vessel in order to avoid formation of a vacuum. All the apparatus is mounted in a small box (of the same type as the Ors apparatus). A drip pan should be fitted under the apparatus to catch any mercury which might spill.

An evaluation of the accuracy of the determination of nitrogen by means of this apparatus may be made on the basis of the following considerations. Analytical error during the process of absorbing nitrogen can arise from insufficient removal of excess hydrogen during saturation of the magnesium (calcining at 800° for 1 hour before analysis) or from the presence of oxygen-containing compounds in the hydrogen used. At 800°, oxygen, CO_2, etc. react with hydrogen and saturated hydrocarbons so that the final volume of the mixture is changed. This must always be taken into account.

Usually for a measuring buret of 5 ml capacity graduated to 0.05 ml, readings can be taken with an accuracy of 0.02-0.025 ml. Consequently for such an accuracy the absolute error of the apparatus is equal to 0.02-0.025 ml and the relative error in this case (assuming a total volume of 5 ml) will be 0.5%.

Since it is more expedient to determine the nitrogen after absorption of CO_2, unsaturated hydrogen, O_2 and CO i.e. to determine it from the remaining mixture of gases consisting usually of hydrogen, saturated hydrocarbons and nitrogen, then the value of the relative error with respect to the total residue increases somewhat.

But if it is taken into account that the hydrogen and saturated hydrocarbons in another sample of the test mixture are determined by combustion with an accuracy of up to 0.2-0.3%, then on comparing the result of both analysis (for nitrogen on the one hand and hydrogen and saturated hydrocarbons on the other) the maximum error as shown experimentally amounts to 1% i.e. within the limits of the errors of normal gas analysis.

SUMMARY

We have designed an apparatus which is based on a chemical method for the determination of nitrogen indicated by A.P.Lidov. The analytical technique for the analysis of mixtures left after the usual absorptions is more simple, and the

apparatus designed in such a way that it is incomparably more portable than apparatus suggested previously (which have accordingly not been widely adopted) and can be made in any laboratory.

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CHRONICLE

FROM THE CHEMICAL SCIENCES SECTION OF THE ACADEMY OF SCIENCES U.S.S.R.

The Commission on the History of Chemistry from the Chemical Sciences Section of the Academy of Sciences USSR has started preparations for convening a Third All-Union Conference on the History of Chemistry which it proposes to hold during 1953.

The chief purpose of the future conference will be the consideration of basic questions connected with the preparation of a text book on the History of Russian Chemistry and monographs on the most important problems in the history of Russian chemistry.

The reports to the conference will be devoted to the following problems:

1. General and methodological problems in the history of chemistry. (Objects, methods, problems, significance of the history of chemistry. The problem of the periodization of the general history of chemistry, periodization of the history of the development of individual branches and divisions of chemistry, periodization of the history of Russian chemistry. Sources of the study of the history of chemistry, criticisms of the work of bourgeois historians of science).

2. The most important stages and paths in the development of chemistry. (History of the development of various nodal problems of Russian chemistry in conjunction with its contemporary position and the perspectives of the development of chemistry. History of the most important directions in the development of chemistry in the Socialist epoch).

3. New facts hitherto unknown and not published in the literature on the discoveries of Russian scientists. The priority of important discoveries of Russian scientists.

The Commission invites participation in the work of the conference.

The subjects of reports or communications should be sent not later than November 1st, 1952.

The Commission at the same time wishes to state that apart from the publication of the proceedings of the conference it intends to issue a Symposium on the Proceedings of the Commission in which various reports heard at the meeting will be published in addition to works of a research nature on the history of chemistry carried out in Academic or Non-academic Institutions.

Articles and communications for inclusion in the next issue of the Symposium on the History of Chemistry must be sent not later than Nov. 1st, 1952.

Any enquiries should be addressed to: Moscow, Bolshaya Kaluzhskaya Dom 31, Comissiya Po Istorii Khimii Otdeleniya Khimicheskikh Nauk, Acad. Nauk, USSR.

Commission on the History
of Chemistry.

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CARRY THE BANNER OF SOVIET SCIENCE PROUDLY

The historical resolutions of the XIX Congress of the Communist Party of the Soviet Union open up new, boundless horizons for scientific and practical activity before the analytical chemists of our country.

The gigantic developments of industry provided for by the directives of the Congress, the huge increase in work on the study of the mineral resources of our country, and the use of its immense natural resources, the construction of the colossal undertakings for the production of energy, the increase in agricultural production and much else - all require a considerable increase in analytical chemical work, the setting up of new analytical laboratories; it is necessary to solve a number of new problems in science, to improve available methods of analytical control already in use and to develop new ones; to construct new apparatus, to discover new reagents; to examine existing theoretical principles critically, and to develop new theories in analytical chemistry in the light of dialectical materialism; to produce special textbooks and monographs on analytical chemistry.

The necessity of satisfying the analytical requirements of all sections of our socialist economy places an honorable and responsible task before Soviet analysts.

It is essential to develop both the theoretical and practical analytical chemistry of low concentrations of elements - the chemistry of traces. It is essential to develop methods for the separation and concentration of elements from their very dilute solutions - extraction methods, the application of ion exchange resins and of radioactive indicators, etc..

Much contemporary analytical chemistry is far from satisfactory with respect to the rapidity with which an analysis can be carried out. The development of new and the improvement of existing rapid methods of analysis is one of the most important problems of our analysts. Despite the widespread introduction of physical and instrumental methods of analysis, the development of purely chemical, preparatory operations and methods of analysis should not be ignored. In the field of physical and physico-chemical instruments, complex work and further improvements and developments of new forms of available apparatus comes first. It is necessary to introduce automatics positively into analytical chemistry, and to develop automatic and semi-automatic apparatus for chemical analysis.

Our analysts have discovered many new analytical reagents, mainly organic reagents, many of which are nowadays used in analytical laboratories all over the world. It is necessary to continue this glorious tradition of Russian analysts and to discover new analytical reagents on the basis of the theory of their action developed by Soviet scientists, and to continue to develop their theory.

Although there are numbers of fine examples of newly developed analytical methods being rapidly introduced into practice, there are still many cases where this is not true.

In such cases it is necessary to deal resolutely, remembering that there is no point in working out an analytical method which cannot find practical application.

One of the reasons which hinders the introduction of better methods is the lack of a sufficient amount of coordinating work on analytical chemistry between Institute and Factory laboratories, and another is the sometimes unsatisfactory state of the organization of technical information.

We must first of all raise the cultural level of the workers in chemical-analytical, and control laboratories in our factories and set up research groups of analytical chemists in our large factories.

It is necessary to attract more average chemical personnel with a good specialist background for carrying out established analytical control operations. Highly qualified analysts should be given chances to improve their knowledge by means of specialist courses.

During the fifth Five Year Plan the number of young specialists will increase considerably. A large army of young specialists will enter analytical laboratories and Institutions. Older analytical chemists should consider it an honorable task to help these young analysts to organize their work correctly.

Chemical industry and the apparatus manufacturers should satisfy the new requirements of chemists, research workers, and others.

The advance of our science will be slow if we do not maintain a creative exchange of opinion and keep up criticism and self criticism as Comrade Stalin has often pointed out to us.

The Communist party and the Soviet Government show immense trust and support for the scientists of our country. In its directive the XIX Congress remarks:

"Assist the scientist in every way to develop his theoretical problems in all branches of knowledge and strengthen the bond between science and production".

By active, selfless work on his part the Soviet analytical chemist should promote the solution of the miscellaneous problems which crop up as a result of the Five Year Plans and speed up the fulfilment of the Stalin program for the gradual transition from Socialism to Communism.

Soviet analysts must respond with all their strength so that they can repay honorably the trust placed in them, and proudly carry the banner of Soviet science in order that Soviet analytical chemistry together with Soviet science may occupy the first place in the world.

THE APPLICATION OF MATHEMATICAL STATISTICS IN ANALYTICAL CHEMISTRY

N.P.Komar

A. M. Gorky Kharkhov State University

The directives of the XIX Congress of the party regarding the fifth Five Year Plan for the development of the USSR in the period 1951-1955 have placed a number of new and important problems and tasks before the chemists of our country. The fulfilment of these new problems is impossible without a scientifically organized control of all productive operations and in this sense every line of the directives is full of deep import for both those chemists participating directly in production control, and those working out the principles and theoretical details of the theory of analytical chemistry, and new analytical methods.

In the epoch of the great Stalin projects, analysts will have to solve the problems which confront them more accurately and more rapidly than hitherto. Our responsibility for the quality of our work will increase daily and we shall have to adopt all measures possible to improve our work.

In particular it is very important to use the methods of mathematical statistics and the theory of errors on an even wider scale, since they can be of immense value for the selection of new analytical procedures and their development, for the evaluation of analytical results and for the organization of the control of work of any analytical laboratory in the USSR.

The use of mathematical statistics in analytical chemistry is fundamentally sound, since an analyst's work is the sum total of a number of similar operations; weighings, titrations, determinations of optical density, etc.. In order to carry out these operations, various types of apparatus are used, among which it is possible to distinguish individual combinations of similar apparatuses, e.g. analytical weights, pipets, burets, etc.. In this connection also it may be stated that the analyst's work belongs to a number of mass phenomena which can be subjected to statistical investigations.

In so far as the result of every analytical determination can be considered as the sum of a large number of mutually independent items: operations of weighing, measuring volumes, precipitations, filtrations, etc., each of which is subject to the effect of multiform conditions, it is usually possible to assume that the random errors of all normal chemical methods of analysis obey the law of normal distribution:

$$f(x,\sigma) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-a)^2}{2\sigma^2}} , \qquad (1)$$

where a is the true value of the quantity determined, x – the value obtained by a given measurement, e – the base of the natural logarithms and σ^2 – the variance which is equal to the sum of the squares of the deviations of the observations from their mean divided by the number of observations, calculated according to the formula:

$$\sigma^2 = \frac{(x_1-\bar{x})^2+(x_2-\bar{x})^2+\cdots+(x_n-\bar{x})^2}{n} = \frac{\sum_{i=1}^{n}(x_i-x)^2}{n} . \qquad (2)$$

The square root of this quantity is called the mean square deviation of an

individual result from the arithmetic mean or the standard deviation.

In formula (2) n is the number of measurements made in order to determine the arithmetic mean x, which in turn is calculated from the formula

$$\bar{x} = \frac{x_1 + x_2 + \ldots + x_n}{n} = \frac{\sum_{i=1}^{n} x_i}{n}. \quad (3)$$

By means of the equation expressing the law of normal distribution (1) it is possible to calculate the probability of the occurrence of an error in measurement $x - a$, if a and σ^2 are known. For practical purposes however it is much more important to have a sufficiently reliable evaluation of the probability that in any determination of a quantity a, the deviation of a random result x, i.e.,the value of $x - a$ does not exceed some given value t. The respective values of the probability $P_{0,t}$ that the error does not exceed the limits [0, t] are calculated by means of the probability integral:

$$\Phi(z) = \frac{1}{\sqrt{2\pi}} \int_0^z e^{-t^2} 2\,dt = P_{0,t}, \quad (4)$$

which as Equation (4) shows is a function of its upper limit z. Tables for the probability integral written in formula (4) can be found in textbooks on the theory of probability [1,2]. In using such tables $z = t/\sigma$ is taken as the argument, where t is the limit of the interval and σ is the mean square deviation of the result. Similar tables in some textbooks on mathematical statistics [3,4] are compiled for the double interval $[-t,t]$ and differ from (4) by the factor 2; when $z = t/\sigma$ is substituted, the value of $\Phi(z)$ given in such tables gives $P_{-t,t}$ the probability of a random error $x - a$ occurring in the interval $[-t,t]$. The same probability is given by tables [5,6,7,8] for the function

$$\Phi(z) = \frac{2}{\sqrt{\pi}} e^{-t^2} dt = P_{-t,t}, \quad (5)$$

the argument of which is the quantity $z = \frac{t}{\sigma\sqrt{2}}$.

As the tables show, the value of the probability integral expressed by formula (4) tends to 0.5 as z increases, while for the remaining formulas it tends to unity.

Already for $t = 3\sigma$ the value of $P = \Phi(3) = 0.997$ shows that 997 measurements in every 1000 give results which do not overlap the limits $[a - 3\sigma, a + 3\sigma]$. It is because of this that σ^2 plays such an important part as the characteristic of scattering, while the "three sigmas" rule is constantly used in practice because it enables the interval to be determined within the limits of which it is possible to get the true value of the quantity being determined with a probability (reliability) approaching unity.

Unfortunately all the formulas adduced above include the true value of the quantity being determined and they are deduced on the assumption that the number of measurements made is so large that the distribution curve (1) is continuous. In actual analytical practice the number of measurements made is very small and the true value a is the value sought, and must be determined in spite of the large gaps in the series of measurements.

Under these conditions all the purport of the application of the theory of errors to cases of analysis involving only a small number of individual measurements is based on the following ideas:

Let us assume that in all, three measurements of a given quantity have been made and that the results obtained do not differ widely. It is evident that such a coincidence can occur even in the two following extreme cases.

1. All three measurements simultaneously include coarse errors which occur as the result of elementary errors acting on the three results in the same direction.

2. All three results belong to the most probable groups of results i.e., include only small errors.

The probability of the first case is very small, since the probability of a result with a large random error is very small, so that the probability of all three results including large errors is equal to the product of three such low probabilities, i.e. the final probability is also very low.

The probability of the second case is very much higher since it is equal to the probability of getting the most frequent result sufficiently close to the quantity to be determined, a.

An approach of this type to an explanation of the convergence of the results of a comparatively small number of measurements leads to the important conclusion that the most probable result for any group of independent measurements is the arithmetic mean $\bar{x}$ calculated by formula (3) since the sum of the squares of the deviation of the results of separate measurements from their arithmetic mean has a minimum value.

This means that it is precisely by such a choice of the most probable value of the determined quantity that the deviation of $x_i - \bar{x}$ approaches most closely to the ideal distribution curve.

It was found that the arithemtic mean in the general case is not equal to the exact value of a, since

$$\bar{x} = a - \frac{\sum_{i=1}^{n} u_i}{n}, \qquad (6)$$

where $u_i = x_i - a$, i.e. represents the true error of the measurement. From equation (6) it follows that $\bar{x} \to a$ the greater the number of measurements n, and the equation $\bar{x} = a$ is realized only at $n = \infty$. It appears that the real true errors are distributed by the normal law, and their variance σ_u^2 can be calculated according to the formula:

$$\sigma_u^2 = \sigma^2 \frac{n}{n-1} = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}. \qquad (7)$$

The square root of this quantity, viz, σ_u, is called the mean square error of an individual determination.

It has been established moreover that the variance of the mean square $\sigma_{\bar{x}}^2$ is n times less than the variance of the true error σ_u^2 which means that

$$\sigma_{\bar{x}}^2 = \frac{\sigma_u^2}{n} = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n(n-1)} \qquad (8)$$

The square root of this quantity is called the mean square error of the mean value.

These formulas are of immense significance since they give the value of σ by means of which it is possible to find the argument of the probability integral $\Phi(z)$ and to determine with a given probability the limits within which a lies. Nevertheless the direct use of function $\Phi(z)$ is only possible if the number of individual measurements n is so large that the values of σ^2 found in this way are practically the same as σ^2 for $n = \infty$, which is called the variance of the general aggregate, in contrast to the so-called estimate of variance s^2, calculated by the same formula for any values of n.

In so far as $\bar{x}$ and s^2 are determined directly from experimental results it is to be expected that a method can be found for the determination of the sought for value of a by means of their values for any n. This problem is one of the three fundamental problems of mathematical statistics which can be formulated as follows.

1. The value of σ^2 is known and it is necessary to evaluate the unknown value of $\underline{a}$, i.e. to find $\underline{a}$, the values of $[\beta_1, \beta_2]$ (confidence limits) between which the true value of $\underline{a}$ is to be found and the reliability α, i.e., the probability that the true value a lies in the interval $[\beta_1, \beta_2]$.

2. The value of $\underline{a}$ is known and σ^2 remains to be determined.

3. Both $\underline{a}$ and σ^2 remain to be determined.

All these problems have been solved since it was successfully shown that for cases where the distribution of $\underline{x}$ in the general aggregate is normal and has a mean $\underline{a}$, the distribution of the quantity

$$t_1 = \frac{|\bar{x} - a|}{s_{\bar{x}}} \tag{9}$$

for any $\underline{n}$ follows Student's law exactly. According to this law the probability of the value of the quantity t_1 lying between t_1 and $t_1 + dt$, is expressed by the formula

$$P_{t_1, t_1+dt} = c \left(1 + \frac{t_1^2}{k}\right)^{-\frac{k+1}{2}} dt, \tag{10}$$

where $\underline{c}$ is a constant and $\underline{k} = \underline{n} - 1$ is the so called number of degrees of freedom.

Special probability tables have been compiled $P(|t|) \geqslant t_1)$ according to Student's distribution [9] in which are given the probabilities for values of $\underline{t}$ which are not less in numerical value than a given number, if $\underline{x}$ and $s_{\bar{x}}$ are determined for an amplitude $\underline{n}$, i.e. on the basis of the results of $\underline{n}$ individual independent measurements; $x_1, x_2, \ldots, x_n$ that correspond to $\underline{k} = \underline{n} - 1$ degrees of freedom.

Like all other distributions used in mathematical statistics, the $\underline{t}$ distribution assumes only random deviations $x_i - \bar{x}$. Thus for $t_1 = 4.5$ at $\underline{k} = 5$ we find in the table a probability of 0.006, that is usually written in the form $P(|t| \geqslant 4.5) \leqslant 0.006$ or $P(-4.5 < t_1 < 4.5) = 1 - 0.006 = 0.994$. This result can be interpreted as follows; it expresses the probability that the function t_1 for $\underline{k} = 5$ is either equal to or greater than 4.5 as a result of the occurence of only random errors in the measurements $x_1, x_2, \ldots, x_n$ is equal to 0.006, i.e., it is very small. This enables us to conclude that t_1 attains the value of 4.5 not accidentally but as the result of some systematic deviation of the value x_i, i.e. of $\bar{x}$ from $\underline{a}$.

The same table can also be used for evaluating the interval $[\beta_1, \beta_2]$ within the limits of which the true value of the determined quantity α lies with a probability of $\underline{a}$. If it is arranged that the probability $\alpha = 0.95$ for $\underline{k} = 8$ then it is necessary to find t_1 from the table for which $P(|t| > t_1) = 1 - 0.95 = 0.05$ (in the given case $t_1 = 2.3$). Substituting this value in formula (9) it follows that

$$a = \bar{x} \pm t_\alpha s_{\bar{x}} = \bar{x} \pm \epsilon_\alpha. \tag{11}$$

Here α is the reliability, $\epsilon_\alpha = t_\alpha s_{\bar{x}}$ the accuracy of the approximation equation $\bar{x} \approx a$ and $[\bar{x} - \epsilon_\alpha, \bar{x} + \epsilon_\alpha]$ the confidence limits for the value.

It is obvious that (11) replaces the "three sigmas" rule for analyses involving only a small number of samples ($n \geqslant 2$).

Special tables [10,11,12] exist for the determination of values of t_α for values α equal to 0.9, 0.95, 0.98, 0.99 and 0.999 and different values of $\underline{k} = \underline{n} - 1$. By means of these tables, knowing $\underline{k}$ and assigning a definite value of α, the value of $\underline{t_\alpha}$ which enters into formula (11) can be found directly.

Cases are often observed where the analytical results of the same sample

carried out by two different laboratories, or in the same laboratory by different operators, or by different methods, or simply at different times are characterized by different variances.

In such cases the question arises as to whether the variances differ in a random manner or whether the variances can be traced to serious causes such as poor organization in the laboratory where the variances are highest, or poor reproducibility of results obtained by one of the methods, or differences in operating techniques, or appreciable changes in the quality of the work at different stages of an analytical process.

In cases of this type the ratio of the estimates of variance is used for comparison

$$T_H = \frac{s_1^2}{s_2^2}, \qquad (12)$$

in the numerator of which the greater estimate of variance s_1^2 or s_2^2 calculated by formula (7) is always placed. The value of T_H is greater the greater the divergence of the estimates of variance. Let us assume that our s_1^2 and s_2^2 are variances of a random choice, belonging to one Universe. In this case the differences between them can be explained only by the fact that for the determination of s_1^2 and s_2^2 only a limited number of measurements were made, say n_1 and n_2. It is evident that as n_2 and n_1 increase both estimates of variance will tend to the same value σ^2 and their ratio T_H to unity. For a limited number of measurements the value of T_H can deviate from unity as a result of random variations, and is greater the less n_1 and n_2, which means k_1 and k_2. As a result of the investigation of the T distribution special tables have been compiled. There are two such tables in V.I.Romanovsky's book [13]. They both include values of T which can occur as the result of random causes, if s_1^2 is obtained for k_1 and s_2^2 for k_2 degrees of freedom. The first of these tables contains values of T_5 calculated with a probability of 0.05, while the second T_1 is calculated on a probability of 0.01.

In Dlin's book [14], in one of the tables in addition, for different k_1 and k_2, values are adduced for $P = 0.05$, $P = 0.01$ and $P = 0.001$. It is clear that the estimates of variance s_1^2 and s_2^2 for which $T > T_5$ besides T_1 and T_{01} ($P = 0.001$) cannot be ascribed to random divergence. In such cases it can be stated that there is a serious reason for this divergence which is the result, e.g., of an incorrect approach to the problem, poor reproducibility of one of the methods etc..

If, e.g., s_1^2 and s_2^2 are estimates of variance for the same analytical method which are obtained at different times in the same laboratory and $s_1^2 \gg s_2^2$, this fact signalizes the breakdown of normal working procedure. In this case it must be remembered that the variance of any method σ^2 is an additive quantity.

$$\sigma^2 = \sigma_\alpha^2 + \sigma_\beta^2 + \ldots + \sigma_\omega^2, \qquad (13)$$

where σ_ν^2 is the variance of individual operations (e.g. weighing etc.). This means that in order to restore normal work it is necessary to explain which of these σ_ν^2 is responsible for the divergence and to eliminate it by controlling the corresponding process.

Finally in a number of cases, the analyst must assess the variance of the method which can be evaluated as the variance of the Universe σ^2, from the results of a small number of analyses n which only enables the estimate of variance s^2 to be calculated. This problem can be solved with a sufficient degree of approximation by means of the inequality

$$s - \frac{3s}{\sqrt{2(n-1)}} < \sigma < s + \frac{3s}{\sqrt{2(n-1)}}, \qquad (14)$$

which determines the confidence limits of the required variance of the method.

The inequality (14) is compiled according to the "three sigmas" rule because the mean square deviation for the mean square deviation itself, i.e. s_s, can be determined sufficiently accurately by means of the formula

$$s_s = \frac{s}{\sqrt{2(n-1)}} \tag{15}$$

It very often happens that in the investigation of new standard samples the work is entrusted to a few analysts or laboratory assistants each of whom gives a series of values for the quantities being determined and the respective arithmetic mean, and variance. If subsequent analysis of these results show that the deviation between individual means and variances can be related to random errors, then the new, corrected value of the mean is calculated by the formula:

$$\bar{x} = \frac{n_1\bar{x}_1 + n_2\bar{x}_2 + \ldots + n_p\bar{x}_p}{n_1 + n_2 + \ldots n_p} = \frac{\sum_{\alpha=1}^{p} n_\alpha\bar{x}_\alpha}{\sum_{\alpha=1}^{p} n_\alpha}, \tag{16}$$

where $\bar{x}_1$ is the mean in the first series of measurements with amplitude n_1, etc..

If further for the same p series of measurements, the amplitudes of which are respectively equal to $n_1, n_2, \ldots, n_p$, the means found $\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_p$ and the estimates of variance $s_1^2, s_2^2, \ldots, s_p^2$, then for the whole aggregate of $n_1+n_2 \ldots+n_p = \Sigma n_\alpha$, the measurements of the estimates of variance s^2 are determined by the formula;

$$s^2 = \frac{n_1s_1^2+n_2s_2^2+\ldots+n_ps_p^2}{\sum n_\alpha} + \frac{n_1(\bar{x}_1 - \bar{x})^2+n_2(\bar{x}_2 - \bar{x})^2+\ldots+n_p(\bar{x}_p - x)^2}{\sum n_\alpha}$$

or

$$s^2 = \frac{\sum_{\alpha=1}^{p} n_\alpha s_\alpha^2}{\sum_{\alpha=1}^{p} n_\alpha} + \frac{\sum_{\alpha=1}^{p} n_\alpha(\bar{x}_\alpha - \bar{x})^2}{\sum_{\alpha=1}^{p} n_\alpha}, \tag{17}$$

where $\bar{x}$ is determined by formula (16).

The information given above is sufficient for consciously using the methods of mathematical statistics for normal analytical work. These methods are illustrated below by a number of examples taken from analytical practice. Special formulas which are often used for similar purposes [15,16] are obtained on the basis of the same fundamental considerations outlined above.

Calculations which must be used to carry out a statistical treatment of analytical results reduce to a determination of the arithmetic mean and the variance. The arithmetical calculating part of the work can be simplified considerably by means of the following formulas:

$$\bar{x} = c + \frac{\sum_{i=1}^{n} (x_i - c)}{n}, \tag{18}$$

$$\sum_{i=1}^{n} (x_i - \bar{x})^2 = \sum_{i=1}^{n} (x_i - c)^2 - n(c - \bar{x})^2, \tag{19}$$

$$\sum_{i=1}^{n} (x_i - \bar{x})^2 = \sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i\right)^2}{n} \tag{20}$$

In formulas (18) and (19), c is any number, but it is convenient to choose it so that it does not differ very much from the actual arithmetic mean and is also convenient for calculating the differences $x_i - c$. When using formulas (18) and (19) for numbers on which it is necessary to operate, the number of signs can be reduced considerably; subsequent determination of the differences in squares can be done mentally or with the help of a small table of squares.

Formula (20) is suitable in those cases where the original x_i includes a small number of signs; otherwise Barlow's tables must be used.

Present day analysts in whatever laboratories they work often have to solve the following problems.

1) To choose the best of two published methods for determining the same thing.

2) To use a chosen analytical method, i.e., to find the amount of some compound in a test sample with a fair degree of accuracy and to evaluate this approximation, having eliminated spurious results.

3) To analyze the results obtained in order to explain their stability to random effects and to eliminate possible systematic errors.

4) To present the results obtained in such a form that anybody entrusted to carry out a similar analysis gets not only the figures characterizing the percentage of compound to be determined in a sample but also an exact idea of the reliability of the result.

Analysts concerned with developing new methods should in this connection give all the results in their articles so that any chemist can use the new method in the most rational manner.

Every article should therefore contain:

1) a detailed description of all the precautions and apparatus which the author of the article used so as to show that the recommended method does not include systematic errors.

2) information on results obtained by means of the new method for varying initial concentrations of the test compound.

3) results characterizing the systematic errors of the method in the presence of other materials.

Every investigation of this type includes a number of separate analyses and measurements, but no journal is prepared to publish all the results. In this connection therefore authors usually publish only an insignificant amount of all their numerical data, which in their opinion is sufficient to evaluate the method, and leave out as a consequence a number of results which lower the value of a particular piece of work.

By adopting a statistical treatment of the results of such research work, all the material accumulated can be made accessible to the reader in the form of a few figures which characterize:

1) the value of n (the number of anlyses) or $k = n - 1$,

2) the value of the estimate of variance s^2 or the variance σ^2;

3) the value of the accuracy $\epsilon_\alpha = t_\alpha s_{\bar{x}}$ with an indication of the probability adopted α;

4) the confidence limits which determine the systematic errors;

5) the relation between the variance of the method and the initial concentration of the test compound;

6) the relation between the variance of the method and the concentration

of any other ions in the system.

Such an approach to formulating the work done facilitates the introduction of new analytical methods, since the practising analyst having read the article will be in possession of all the results characterizing the method.

At the same time the feeling of responsibility on the part of the author increases since the statistical characteristics $\bar{x}$ and σ^2 are much more reliable than the individual measurements hitherto published and should be capable of being repeated by anyone.

Information about standard samples should also contain the accuracy of each $\varepsilon_\alpha = t_\alpha s_{\bar{x}}$ with an indication of the reliability and also the values of $k = n - 1$ and s^2, since in the absence of these results, a decision on the question of the "non-coincidence of results with the normal" becomes impossible.

The examples quoted below are taken from Russian chemical journals, major attention being given to the question of evaluating a new method and comparisons of the various methods.

A. A General Evaluation of a Method from the Results Obtained by Using it for Samples whose Compositions are Already Known

In Zolotukhin's paper [18] results are given for four acidimetric determinations of beryllium in a test containing 2.655 mg equivalents of $BeSO_4$. In table 1 these results are treated statistically, it being assumed that the initial value of 2.655 mg equivs. does not contain any errors although there is no proof of this in Zolotukhin's article. Calculations of $\bar{x}$ are carried out by means of (18), of $\Sigma(\bar{x}_1 - \bar{x})^2$ by (19) and finally the divergence between a = 2.655 and $\bar{x}$ = 2.6465 mg equivs. is investigated by means of formulas (9) and (11) and Student's tables of distribution [9].

From table 1, t_1=3.27 for $k = 4 - 1 = 3$. In the probability tables $P(|t| \geqslant t_1)$ calculated according to Student [9] we find that $P(|t| \geqslant 3.2)$=0.048 and $P(|t| \geqslant 3.3)$ =0.045. Simple interpolation gives $P(|t| \geqslant 3.27)$=0.046. This result is used as follows.

1. The value of t_1 is found from formula (9), assuming that the deviation between the value of a and $\bar{x}$ depends on various random causes.

2. It was found that t_1=3.27 and that the probability of the occurence of a value of $t \geqslant 3.27$ for $k = 3$ is equal to 0.046.

3. If it is arbitrarily agreed to split up all the values of t_1 which occur only as a result of random causes into those of low probability, i.e., those rarely met, and those which turn up pretty often, and to relate to the low probability group all those t_1's for which $P(|t| \geqslant t_1) < 0.05$, then it must be accepted that the value of $t_1 = 3.27$ has occured as the result of systematic errors.

TABLE 1

Investigation of the results of acidimetric determination of $BeSO_4$ by V.K.Zolotukhin's method
a = 2.655 mg equiv. $BeSO_4$

No.	$BeSO_4$ found x_1	$(x_1 - 2.645)\cdot 10^3$	$(x_1 - 2.645)^2 \cdot 10^6$
	mg. equiv.		
1	2.649	4	16
2	2.640	-5	25
3	2.645	0	0
4	2.652	7	49
Total		$6\cdot 10^{-3}$	$90\cdot 10^{-6}$

$$\bar{x} = 2.645 + \frac{6\cdot10^{-3}}{4} = 2.645 + 1.5\cdot10^{-3} = 2.6465;$$

$$\sum_{i=1}^{4} (x_1 - \bar{x})^2 = 90\cdot10^{-6} - 4(1.5\cdot10^{-3})^2 = 81\cdot10^{-6};\ s^3 = \frac{81\cdot10^{-6}}{4-1} = 27\cdot10^{-6};$$

$$s_x = \sqrt{\frac{81\cdot10^{-6}}{4(4-1)}} = 2.6\cdot10^{-3};\ t_1 = \frac{|2.655 - 2.6465|}{2.6\cdot10^{-3}} = \frac{8.5\cdot10^{-3}}{2.6\cdot10^{-3}} = 3.27$$

4. In order to evaluate the systematic errors, the value of $t_{0.95}$ for $k = 3$ is found and substituted in the formula (9); from this it follows that $\bar{x} - a = \pm 3.16.\ 2.6\cdot10^{-3} = \pm 8.2\cdot10^{-3}$.

5. It is obvious that the systematic error $E = \bar{x} - a$ is evaluated with the same accuracy $\pm 8.2\cdot10^{-3}$, i.e., that with a reliability of 0.95 it can be asserted that E is included in the interval $[8.5\cdot10^{-3} - 8.2\cdot10^{-3},\ 8.5\cdot10^{-3} + 8.2\cdot10^{-3}]$ or $[3\cdot10^{-4},\ 1.7\cdot10^{-2}]$. This interval is very big but by increasing the number of titrations it should be possible to decrease it. We do not know how many measurements V.K.Zolotukhin made; one thing is however, clear, viz., the results given in the article are insufficient to form a judgement of the method.

If Zolotukhin had treated his results statistically then for any number of experiments n he could have characterized his results in one line instead of in a whole table. All he would have had to write would be the values of a, n, $\bar{x}$, s^2, $s_{\bar{x}}$, t_1, $P(|t| \geqslant t_1)$, t_α, $t_\alpha s_{\bar{x}}$ and $E = a - \bar{x}$.

An analyst reading the article containing this information would get a complete picture of the method and could evaluate $s_{\bar{x}} = \frac{s}{\sqrt{n}}$ in particular for any number of tests n, i.e. the relative probable error of the method

$$\pm \frac{t_\alpha s_{\bar{x}} \cdot 100}{a\sqrt{n}}, \tag{21}$$

B. Evaluation of the Effect of Other Components

In Naumov's paper [19] the effect of ethylene oxide on the optical density (D) of m-phenylendiamine in its mixtures with acetaldehyde was investigated. In Table 2 results of the statistical treatment of the results from Table 3 of Naumov's paper are given. In this case instead of $\bar{x}$ and the value of a, which is regarded as reliable, it is necessary to compare the mean values of the two series of experiments, i.e. the values of $\bar{x}_1$ and $\bar{x}_2$. For this purpose the following formulas are used:

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\bar{x}}}, \tag{22}$$

$$s_{\bar{x}} = s\sqrt{\frac{n_1 + n_2}{n_1 n_2}}, \tag{23}$$

$$s = \sqrt{\frac{\sum_{i=1}^{n_1} (x_{1i} - \bar{x}_1)^2 + \sum_{j=1}^{n_2} (x_{2j} - \bar{x}_2)^2}{n_1 + n_2 - 2}}, \tag{24}$$

$$k = n_1 + n_2 - 2, \tag{25}$$

TABLE 2

The effect of ethylene oxide on the optical density (D) of m-phenylendiamine in its mixtures with acetaldehyde.

No.	CH_3CHO in %	$(CH_2)_2O$ in %	D_i	$(D_i - \bar{D}) \cdot 10^2$	$(D_i - \bar{D})^2 \cdot 10^4$	s^2	$\bar{D}_s$
1	0.051	0.00	1.22	2	4		
2	0.051	0.00	1.17	-3	9		
3	0.051	0.00	1.18	-2	4		
4	0.051	0.00	1.23	3	9		
			$\bar{D}_1$ = 1.20		$26 \cdot 10^{-4}$	$8.7 \cdot 10^{-4}$	$1.48 \cdot 10^{-2}$
1	0.051	1.50	1.26	2	4		
2	0.051	1.50	1.22	-2	4		
			$\bar{D}_2$ = 1.24		$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$2.00 \cdot 10^{-2}$
1	0.051	2.35	1.28	-0.5	0.25		
2	0.051	2.25	1.29	0.5	0.25		
			$\bar{D}_3$ = 1.285		$0.5 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$	$5.00 \cdot 10^{-3}$
1	0.051	4.50	1.34	-3	9		
2	0.051	4.50	1.40	3	9		
3	0.051	4.50	1.37	0	0		
			$\bar{D}_4$ = 1.37		$18 \cdot 10^{-4}$	$9 \cdot 10^{-4}$	$1.73 \cdot 10^{-4}$

where $\bar{x}_1$ is the mean for the first series of analyses, etc., and x_{11} the individual results of the first series of analyses etc

1. First the compatibility of the results of all four series must be tested. In order to do this it is sufficient to compare the extreme values of s^2: $s_4^2 = 9 \cdot 10^{-4}$ and $s_3^2 = 0.5 \cdot 10^{-4}$ for $k_4 = 2$ and $k_3 = 1$. Using formula (12) and the table of T distributions [13] we find that $T_H = s_4^2/s_3^2 = 18$ is much smaller than the tabular value of T for the same $\underline{k}$, which is equal to 199.5. It is obvious that the greatest divergence in the variances between individual series of Naumov's results are completely explained by random errors.

2. Using formulas (24), (23), and (22) for the first two series of experiments we get $\underline{s} = 2.92 \cdot 10^{-2}$, $s_{\bar{D}} = 2.53 \cdot 10^{-2}$, $\bar{D}_1 = 1.20$, $\bar{D}_2 = 1.24$, $t_1 = 1.59$. Further in the Student's tables of [9] distribution we find that for $\underline{k} = 4 + 2 - 2 = 4$ $P(|t| \geqslant 1.6) = 0.185$. This means that the probability of the occurence of a value $t = 1.59$, only as a result of random errors is so great that it is impossible to ascribe the small increase in $\bar{D}_2$ to the presence of 1.5% ethylene oxide.

3. A similar treatment of the results of the first and third series leads to the following values: $\underline{k} = 4$, $\underline{s} = 2.58 \cdot 10^{-2}$, $s_{\bar{D}} = 2.23 \cdot 10^{-2}$ $[\bar{D}_1 - \bar{D}_3] = 8.5 \cdot 10^{-2}$, $t_1 = 3.82$ and $P(|t| \geqslant 3.82) = 0.019$. The probability found is less than 0.05; it is impossible therefore to attribute the value of $t_1 = 3.82$ to random errors, and it must be accepted that systematic changes occur in the optical density as a result of the presence of ethylene oxide.

In order to evaluate the confidence limits we find t_α by the tables [10,11,12], for $\underline{k} = 4$ $t_{0.95} = 2.78$; then $\epsilon_{0.95} = \pm 2.78 \cdot 2.23 \cdot 10^{-2} = \pm 6.2 \cdot 10^{-2}$, and the confidence limits are respectively equal to $8.5 \cdot 10^{-2} - 6.2 \cdot 10^{-2} = 2.3 \cdot 10^{-2}$ and $8.5 \cdot 10^{-2} + 6.2 \cdot 10^{-2} = 14.7 \cdot 10^{-2}$.

4. Finally a comparison of the first and fourth series gives $\underline{k} = 5$, $\underline{s} = 2.97 \cdot 10^{-3}$, $s_{\bar{D}} = 2.27 \cdot 10^{-2}$, $|\bar{D}_1 - \bar{D}_4| = 0.17$, $t_1 = 7.5$ $P(|t| \geqslant 6.0) = 0.002$ and consequently, $P(|t| \geqslant 7.5 < 0.002$, which means that $t_1 = 7.5$ is not accidental. Further for $k = 5$ $t_{0.95} = 2.57$, $\epsilon_{0.95} = \pm 5.8 \cdot 10^{-2}$ and the confidence limits for the value

$E = \bar{D}_1 - \bar{D}_4$ have the values 0.11 and 0.23.

By comparing the limits found [$2.3 \cdot 10^{-2}$, $14.7 \cdot 10^{-2}$] and [0.11, 0.23], it can be affirmed that Naumov should have plotted sections of straight lines in 0.12 units of optical density, instead of points on his graph No. 3.

It is highly possible that Naumov made a far greater number of measurements, since a measurement of D does not require much time, but he has not included these in his article and as a result of reading his paper a number of doubts and questions arise. At the same time by adopting a statistical method of treating the results, he could have represented all his results in the form of one table compiled as follows:

CH_3CHO, %	$(CH_2)_2O$, %	n	$\bar{D}$	$\sum(D_i - \bar{D})^3$	s^2	$s_{\bar{D}}$
---	---	---	---	---	---	---
---	---	---	---	---	---	---
---	---	---	---	---	---	---

All Naumov's results occupying 11 lines in his paper can be written in four lines.

C. Evaluation of a Method by Comparing the Results Obtained by this Method in the Determination of Various Amounts of a Test Compound, With those of Similar Determinations Carried out by Means of a Standard Method.

This type of experiment is often met. When it is used it is assumed that the results x_i obtained by a standard procedure is free from errors. The results y_i obtained by the test method can include errors, and the problem reduces to a determination of random variations during repeated determinations y.

In the articles describing such methods, two series of parallel results, those for x_i and y_i, are given, which cover the concentration range in which the author is interested. Direct statistical treatment of such results is impossible, and therefore an investigation of the ratio y_i/x_i is made instead, since these should maintain their value from one experiment to another.

1. In Table 3, columns 2 and 3, results are adduced from Table 4 of Golubtsova's article [20], which show that the hydrolytic separation of Nb from mineral acid solutions gives the same results as from $HClO_4$ solution. Here x_i are the values obtained with $HClO_4$ which must be regarded as free from errors and y_i are the parallel values for mineral acid media. The values of $z_i = y_i/x_i$, as can be seen from the table, vary around 1.003 and $s = 7.1 \cdot 10^{-4}$ is the practical estimate of variance of y_i since all the values of y_i/x_i lead to $x_i = 1\%$.

An analyst following Golubtsova's method can use the value s^2 as follows. Let us assume that three determinations of Nb were made and that an average content of 2.72% of this element was found. Then $s_{\bar{y}} = s/\sqrt{3}$ and for $k = 2$ $t_{0.95} = 4.30$, which means that the accuracy $\epsilon_{0.95} = \pm t_{0.95} \cdot s_{\bar{y}} = 4.30 \cdot 2.7 \cdot 10^{-2}/\sqrt{3} = 6.7 \cdot 10^{-2}$ %, from which the relative error should not, for a probability of 0.95, exceed in a given analysis $6.7 \cdot 10^{-2} \cdot 10^2/2.72 = 2.5\%$.

The question as to whether the test method includes systematic errors or not must be solved in a more complicated manner [21].

1. The constants a and b of the linear equation $Y = a + bx$, connecting the values of x regarded free from errors with the values which might contain errors Y, are determined in the usual way.

TABLE 3

Results of the hydrolytic separation of Nb in the presence of $HClO_4$ (x_1) and in mineral acid media (y_1)

No.	Nb found in Percent		$\frac{y_1}{x_1} = Z_1$	$(Z_1 - \bar{Z}) \cdot 10^3$	$(Z_1 - \bar{Z})^2 \cdot 10^6$
	x_1	y_1			
1	3.14	3.19	1.0160	+13	169
2	2.63	2.59	0.9846	-18.4	338.56
3	1.26	1.22	0.9682	-34.8	1211.04
4	1.09	1.11	1.0190	+16	256
5	1.06	1.04	0.9810	-22	484
6	0.58	0.60	1.0350	+32	1024
7	0.39	0.38	0.9742	-28.8	829.44
8	0.18	0.19	0.0555	+52.5	2756.25
9	0.17	0.17	1.0000	-0.3	0.09
10	0.16	0.16	1.0000	-0.3	0.09
11	0.08	0.08	1.0000	-0.3	0.09
Total	10.74	10.73	11.0335		$7,069 \cdot 10^{-3}$
Mean	0.9766	0.9754	1.0030		

$$s^2 = \frac{7.069 \cdot 10^{-3}}{10} = 7.1 \cdot 10^{-4}; \quad s = 2.7 \cdot 10^{-2}$$

TABLE 4

Results of the conductometric titration of zinc acetate ($ZnAc_2$) with barium hydroxide

No.	$ZnAc_2$ taken, in mg, x_1	$ZnAc_2$ found, in mg, y_1	$\frac{y_1}{x_1} = Z_1$	$(Z_1 - \bar{Z}) \cdot 10^4$	$(Z_1 - \bar{Z})^2 \cdot 10^8$	X, in mg
1	16.63	16.63	1.0000	-163	26569	16.63
2	11.09	11.12	1.0033	-130	16900	11.09
3	5.54	5.58	1.0075	-88	7744	5.52
4	1.85	1.95	1.0543	380	144400	1.86
Total	35.11	35.28	4.0651		$1,956 \cdot 10^{-3}$	
Mean			1.0163			

$$s^2 = 6.5 \cdot 10^{-4}$$

2. $\sum (y_i - Y_i)^2$ is found and then the estimates of variances s_y, s_a, s_b determined by means of the formulas

$$s_y^2 = \frac{\sum_{i=1}^{n} (y_i - Y_i)^2}{n - 2}, \quad s_a^2 = s^2 \frac{\sum_{i=1}^{n} x_i^2}{n \sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}, \quad s_b^2 = \frac{s^2}{\sum_{i=1}^{n} x_i^2 - \bar{x} \sum_{i=1}^{n} x_i}, \quad (26)$$

where s_y^2 is the estimate of variance of an individual analysis, s_a^2 the estimate of variance of a and s_b^2 the estimate of variance of b.

3. The value of $t_a = \frac{|a|}{s_a}$ and its probability for $k = n - 2$ are found from a Student's distribution table [9]. If when this has been done it appears that the occurence of values of t_a as a result of only random errors has a low probability, then it may be accepted that the method includes a systematic error t_a,

the confidence limits of which are determined by formula (11) for $\underline{k} = \underline{n} - 2$, with the help of values of t_a, which are found in special tables [10,11,12].

4. The compatibility of the variances obtained directly and indirectly by investigating the ratio $y_i/x_i = z_i$, since for a case of large divergence, it is to be expected that the value of the variance, will change with the concentration of the test material.

5. Finally the average value of $\overline{y_i/x_i} = \overline{z}$ is compared with the value of the tangent of the straight line $\underline{b}$.

All this work should of course be carried out when the method is tested, but usually authors of new analytical procedures publish only some of their results, presuming apparently that every analyst can get all the characteristics which he needs independently. Golubtsova did not carry out such a statistical treatment. Our calculations show that in this case $\underline{Y} = -0.0028 + 1.002x$, while $s_y^2 = 7.9 \cdot 10^{-4}$, $s_b = 8.6 \cdot 10^{-3}$, $s_a = 1.2 \cdot 10^{-2}$ as a result $t_a = 0.24$. In so far as $P(|t| \geqslant 0.24 = 0.846$, if $\underline{k} = 9$, then it can be stated that $\underline{a} = -0.0028$ is the result of random errors and this means that the straight line should go through the origin. At the same time the value for $b = 1.002$ which is in good agreement with $\overline{z} = 1.003$ s_y^2 with a value of s^2 is derived in Table 3.

All these results show that the hydrolytic precipitation of Nb in mineral acids does not differ in practice from precipitation from $HClO_4$ solutions.

As the second example of this type we shall use the results of Udovenko and Pasovskaya [22] on the conductometric titration of zinc acetate with barium hydroxide. The results for the statistical treatment of the experimental data are given in Table 4.

In this case according to Table 4, $s^2 = 6.52 \cdot 10^{-4}$, while the estimate of variance and the mean square error calculated by formula (24) have the values $s_y^2 = 4 \cdot 10^{-4}$, $s_a = 1.86 \cdot 10^{-2}$ and $s_b = 1.8 \cdot 10^{-3}$. The equation for the straight line in this case is of the form $\underline{Y} = 0.0952 + 0.9940x$, while $t_a = \frac{3.5 \cdot 10^{-2}}{1.86 \cdot 10^{-2}} = 5.12$, and for $k = 4 - 2 = 2P(|t| \geqslant 5.0) = 0.038$, the value of $t_a = 5.12$ cannot therefore be attributed to random errors. By rewriting the equation of the straight line in the form $X = -0.0958 + 1.006y$, it can be used for calculating the required values of $\underline{X}$ which are given in the last column of Table 4.

It is evident that this method gives satisfactory results. It is necessary to note in particular that the estimate of variance $s^2 = 6.5 \cdot 10^{-4}$ calculated from the results of Table 4 differs only very slightly from the estimate of variance $s_y^2 = 4 \cdot 10^{-4}$, calculated by means of formulas (26). This fact shows that in the conductometric determination of ZnAc the variance of the method is practically independent of the amount of test material.

As a third example we shall quote Udovenko's and Pasovskaya's results [23] on the conductometric determination of KCl with sodium picrate. The statistical treatment is given in Table 5.

In this case according to the results in Table 5, $s^2 = 1.22 \cdot 10^{-4}$; the equation for the straight line $\underline{Y} = -2.41 + 1.028x$; calculations by formula (26) give; $s_y^2 = 0.606$; $s_a = 1.15$; $s_b = 1.1 \cdot 10^{-2}$ and $t_a = 2.09$. According to Student's tables of distribution [9] for $\underline{k} = 3$ $P(|t| \geqslant 2.1) = 0.127$. Although this value is small it is still greater than 0.05 which we have hitherto regarded as a provisional limit between normal and rare events, and means that a value of $\underline{a} = -2.41$ must be regarded as arising from random causes. If more results were available the question could be fully solved, but Udovenko and Pasovskaya do not give these very necessary results and the question remains open. If it is accepted nevertheless that the method includes a systematic error and the equation rewritten in the form $X = 2.34 + 0.973y$, then the experimental results can be corrected slightly, as the figures adduced in the last column of Table 5 show.

TABLE 5

Results for the conductometric titration of KCl with sodium picrate

No.	KCl taken, in mg x_i	KCl found, in mg y_i	$\frac{y_i}{x_i} = Z_i$	$(Z_i - \bar{Z}) \cdot 10^5$	$(Z_i - \bar{Z})^2 \, 10^{10}$	X in mg
1	56.20	56.00	0.9964	-586	343396	56.82
2	80.30	79.30	0.9876	-1466	2149156	79.48
3	105.50	105.59	1.0010	-126	15876	105.1
4	120.58	122.23	1.0140	1174	1378276	121.2
5	150.72	152.53	1.0123	1004	1008016	150.6
Total	513.3	515.65	5.0113		$4,895 \cdot 10^{-4}$	
Mean			1.00226			

$$s^2 = 1.22 \cdot 10^{-4}$$

Of special interest in this example is a comparison of the tabular $s^2 = 1.22 \cdot 10^{-4}$ and the estimate of variance calculated for the values of $y - \bar{y}$ by formula (26) $s_y^2 = 0.606$. The ratio of these estimates of variance $T_H = 4970$, while for $k_1 = 3$ and $k_2 = 4$, the probability of T being greater or equal to 16.69 as a consequence of only random causes, is equal to 0.01. This means that $T_H = 4970$ cannot be explained by any random causes; here apparently the variance depends on the amount or concentration of the ion determined. Only the first steps have been made in investigating such systems.

D. The Evaluation of Micro Amounts on a Background of other Factors is Closely Related to the Examples Considered.

Problems of this type are of immense importance in the national economy, and the methods used and the results obtained should therefore be particularly carefully analyzed. As an example we shall consider results on the determination of CO in air by using the red oxide of mercury. This method essentially consists in measuring the loss in weight of a tube filled with HgO as a result of the reaction $HgO + CO \longrightarrow CO_2 + Hg$ at a temperature of 200°. The background in this case is determined by the partial dissociation of HgO at the temperature of the experiment and according to the authors' results [25] is characterized for pure air by the following series of results, calculated on CO: 2.6, 5.6, 5.6, 4.9, 5.0 μg (the values were calculated by us). It is pertinent to ask whether air contains CO when three replicates give results of 7.7, 8.3, and 6.8 μg/liter.

The solution of this question leads to an evaluation of the difference between two means by the formulas (22), (23), (24), and (25).

TABLE 6

Statistical treatment of the results for the determination of CO in air by a method based on the measurement of the loss in weight of a tube containing red HgO

No.	Control tests with pure air in μg CO/liter x_{1i}	$x_{1i} - \bar{x}_1$	$(x_{1i} - \bar{x}_1)^2$	No.	Results of the analysis of air in μg CO/liter x_{2j}	$x_{2j} - \bar{x}_2$	$(x_{2j} - \bar{x}_2)^2$
1	2.6	-2.2	4.84	1	7.7	0.1	0.01
2	5.6	0.8	0.64	2	8.3	0.7	0.49
3	5.6	0.8	0.64	3	6.8	-0.8	0.64
4	4.9	0.1	0.01				
5	5.0	0.2	0.04				
6	5.0	0.2	0.04				
Total	28.7		6.21		22.8		1.14
Mean	4.8				7.6		

$$s = \sqrt{\frac{6.21 + 1.14}{6 + 3 - 2}} = 1.02; \quad s_{\bar{x}} = 1.02\sqrt{\frac{6+3}{6\cdot 3}} = 0.72;$$

$$t_1 = \frac{|4.8 - 7.6|}{0.72} = 3.87; \qquad k = 6 + 3 - 2 = 7;$$

$$p(|t| \geq 3.9) = 0.011$$

The calculations given in Table 6 give a value of $t_1 = 3.87$, the probability of the occurence of which as a result of random causes = 0.011. It is obvious that $t_1 = 3.87$ cannot be regarded as random and the difference between the means $\bar{x}_{1j}$ and $\bar{x}_{2j}$ is explained by the presence of CO in the air analyzed. The required value of the concentration of CO is determined with a reliability of 0.95 in the interval [5.7, 9.5 μg] since $t_{0.95} = 2.57$ for $k = 5$.

All determinations of trace elements and forensic analyses, etc., should be subjected to similar statistical treatment.

The examples given widen the scope of the questions touched upon in Gracheva's article [16] but far from exhaust all the cases of the application of statistical methods in chemical laboratories.

SUMMARY

1. The basic principles of the theory of errors, and mathematical statistics of direct importance for analytical chemistry, are set forth.

2. The fundamental formulas for the necessary calculations are adduced.

3. The characteristics which it is necessary to take into account when using mathematical statistics in analytical chemistry are noted.

4. Examples taken from periodical articles are treated in detail.

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3) See Consultants Bureau translation, p.181

THE ULTRAMICRO METHOD OF CHEMICAL ANALYSIS

PART I

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GENERAL OBSERVATIONS

The development of analytical chemistry during the last ten years has been characterized by the introduction into chemical practice of a new technique which has opened up possibilities of working with small amounts of material.

The ultramicro method of chemical analysis has attained very important scientific and practical significance recently. By means of this method it is possible to work with small volumes, as a result of which very small amounts of material can be studied while still maintaining the usual concentrations of solutions.

In the contemporary state of the development of science and experimental technique ultramicro chemical analysis is a natural continuation of the work of Russian scientists in the field of microchemistry. M.V.Lomonosov [1] was the first to use the microscope for chemical research in 1744. Somewhat later in 1798 the Russian chemist and crystallographer T.E.Lovits [2,3] developed this method of analysis and showed that a drop of solution is sufficeint for the determination of its qualitative composition by the method of microcrystalloscopy. In 1873 N.N.Akhmatov published his paper on "The application of the microscope to chemical research", in which he set forth a microchemical technique for the determination of cations. In 1868 K.A.Timiryazev [4] first introduced into practice gas micro- and ultramicro analysis. In 1929 B.Ormont [5] developed a method for the volumetric ultramicro titration of alkalis and acids. Ultramicro chemical analysis is being developed further in the Soviet Union at present. In particular the work of I.M.Korenman [6,7,8] may be mentioned. The work of the foreign scientists A.Benedetti-Pichler [9] and P.Kirk [10] are also worthy of note.

The great interest focussed recently on ultramicro chemical analysis may be explained by the new possibilities which this method opens up, by means of which very small quantities can be handled. Numerous examples can be quoted in various branches of science where the quantity of test material is so small that it can only be investigated by means of an ultramicro method. By applying this technique it is possible to determine the components of the products of synthesis of minerals at high pressures, which is a very important and interesting problem in experimental geochemistry and mineralogy. The ultramicro method can find a wide application in mineralogy and metallurgy in the analysis of inclusions. The composition of corrosion products can also be studied by means of the ultramicro method. The use of this technique has essential advantages in carrying out biological and clinical investigations. The study of the chemistry of isotopes is a field for the application of this method.

Although based on the same principles as those of the analysis of normal amounts of material the ultramicro method differs essentially in technique and scale. The relative scales of macro, micro, and ultramicro methods are compared in Table 1.

The technique for carrying out chemical operations is different for the ultramicro and macro scales, and even the ultramicro technique itself varies according to the volume containing the test material available. Chemical operations with volumes up to 0.001 ml are carried out with the naked eye or through a magnifying

TABLE 1

Method	Minimum volume of test solution		Minimum weight of element found as a precipitate		Minimum weight of sample for analysis	
	ml	λ	g	μg	g	μg
Macro method	1	1000	10^{-5}	10	10^{-1}	10^{5}
Micro method	10^{-2}	10	10^{-8}	10^{-2}	10^{-3}	10^{3}
Ultramicro method	10^{-6}	10^{-3}	10^{-9}	10^{-3}	10^{-6}	1

glass. Sometimes after carrying out some particular operation the reaction products are observed under the microscope. When the volumes are of the order of 10^{-3} to 10^{-6} ml all the basic operations are carried out on the object stage of the microscope. The tubes used are special forms of micro tubes (Fig.1) with a diameter of 0.5-1.0 mm made from capillaries. Liquids are transferred by means of micro pipets-capillaries with a drawn out end of diameter 0.01-0.02 mm (Fig. 1, 1). The pipet is provided with a piston set up (Fig. 2) for overcoming the surface tension which becomes quite appreciable when working with liquids in capillaries. The high rate of evaporation from small volumes necessitates working in a humid atmosphere which is attained by using a special box (Fig. 3). For the reliable manipulation of the volumes of solution or precipitate which are used in ultramicro chemistry, not only optical apparatus is used (microscope), which gives the impression of working at the scale of normal methods, but also mechanical aids which enable small amounts of material to be manipulated carefully under the microscope. These mechanical aids by means of which the necessary handling operations can be carried out are the movable object stage of the microscope on the one hand and a macromanipulator [9,11] on the other. The microscope and manipulator are both fixed to one plate. The humidity box, with the glass micro tubes (Fig.4) are placed on the object stage of the microscope and the necessary instruments clamped

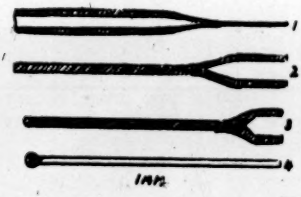

Fig. 1.Apparatus for ultramicro analysis:1 - micropipet; 2 - reaction tubes; 3 - capillary cone; 4 - measuring capillary.

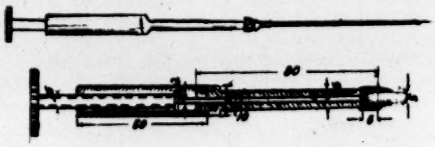

Fig. 2.Piston construction:A - general view (with a micropipet); B - longitudinal section.

in the manipulators. By means of an apparatus set up in this way (Fig. 5) ultramicro chemical determinations can be carried out.

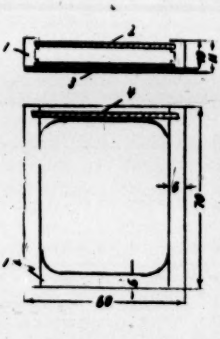

Fig. 3.Box (front view and view from above:1 - brass frame; 2, 3, 4 - glass cover, bottom and side.

Characteristics of the Ultramicro Chemical Method of Analysis

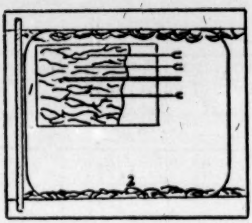

Fig. 4 Humidity Box with micro tube (view from above): 1 - glass plate with tubes; 2 - damp cotton wool.

The ultramicro method is the application of a technique of chemical experimentation which is specific and characteristic to the solution of analytical problems. By means of this technique the problems of the analysis of very small amounts of material can be solved easily and reliably.

Chemical reactions in which only a small number of molecules participates do not differ in any way from reactions in which large amounts of material are involved, as long as the number of reacting molecules ensures statistically the establishment of a chemical equilibrium. From this it follows that the concentration of reagents in the normal methods must be maintained; this is achieved by decreasing the volume when investigating small amounts of material.

Using the law of errors which is determined by statistical conditions and assuming that for a qualitative determination, an error of 10% is acceptable and for a quantitative determination an error of 0.1%, the limiting amount of material which is necessary for carrying out a chemical reaction can be calculated as follows;

$$100\frac{\sqrt{n}}{n} = \text{error in percent} \qquad (1)$$

where n is the number of reacting molecules. For a qualitative determination, assuming an average molecular weight of 60, we get;

$$10^{4}\frac{1}{n} = 10^{2}, \text{ from which } n = 100 \text{ molecules i.e. } \frac{60\cdot 100}{6\cdot 10^{23}} = 10^{-20}\text{g}$$

For a quantitative determination, assuming the same average molecular weight, we get

$$10^{4}\frac{1}{n} = 10^{-2}, \text{ from which } n = 10^{6} \text{ molecules, i.e.,}$$

$$\frac{60\cdot 10^{6}}{6\cdot 10^{23}} = 10^{-16}\ \text{g}$$

With amounts of material in excess of this limit any chemical operation can be carried out; whether this limit is exceeded or otherwise in principle depends on the level of development of experimental technique, and methods of observation. Thus, physico-chemical methods of registering reaction products enables the amount of material needed to be reduced by a much greater amount than visual methods (this applies primarily to volumetric and colorimetric determinations). The introduction of the electron microscope into practice opens up greater possibilities than hitherto of approaching the analysis of the limiting amount of material necessary for ensuring the establishment of chemical equilibrium.

One of the main conditions for carrying out these chemical determinations is the maintenance of the normal concentration of reactants by decreasing the weight and volume respectively. This leads to an increase (as compared with the macro methods) of the relative surface of the solution and the reaction tube, i.e., to

an increase in the surface of unit volume so that the surface decreases to a lesser degree than the volume. Table 2 illustrates this point by actual examples.

TABLE 2

Method	Diameter of tube, cm	Height of tube, cm	Surface of tube, cm^2	Vol. of solution, cm^3	Surface of unit volume, $S_{rel.}$	$\frac{S_{rel.\ ultra}}{S_{rel.\ macro}}$
Macro method	4.0	4.0	62.5	50.0	1.25	>20
Ultramicro method	0.2	0.2	0.16	0.006	26.6	

Since a relatively large surface of contact is established with the tube walls, the dissolved substance is adsorbed on them an also reacts with the material of the wall to a considerably greater extent than in the macro method. As a result, on the one hand there is a loss of part of the test material, and on the other it becomes contaminated. The loss as a result of adsorption on the glass attains very large values for a number of elements in alkaline media. It must also be borne in mind that in practice when using ultramicro techniques it is necessary to concentrate small amounts of material which originally are dispersed in large volumes, in order that one can handle them with the respective technique. In such cases the final solutions which are obtained usually require a preliminary purification from appreciable amounts of other or interfering compounds. These compounds, although at first present only in insignificant amounts – they originate either from the walls of the tube or from the reagents – become concentrated on evaporation. E.g., on evaporating 25 ml of a dilute nitric acid to $5 \cdot 10^{-3}$ - 10^{-2} ml considerable amounts of salts of iron (although the acid was preliminarily distilled), sodium and calcium were obtained as well as a large precipitate of silicic acid (Fig. 6).[1] It is understandable that under these conditions the purity of the original reagents and the stability of the material of the walls of the tube to the effect of the reagents employed acquire a special significance.

The increase in the relative surface which occurs in ultramicro methods in a number of cases affects the velocity of crystallization from solution and the crystal form.

On switching over to the ultramicro scale the free surface of the liquid increases relatively because of the large curvature of the meniscus in the capillaries. As a result the evaporation velocities of solutions which is directly proportional to the free surface of the liquid here attains a considerable value. The evaporation velocity at atmospheric pressure is expressed approximately by the formula

$$v = KS(P - p), \qquad (2)$$

where S - is the free surface of the liquid; P - the pressure of the saturated vapors at a given temperature; p - the pressure of the vapors above the liquid and K - a constant. According to the kinetic theory the change in vapor pressure ΔP with the curvature of the liquid surface is expressed by the equation:

$$\frac{\Delta P}{P} = \frac{2\sigma M}{rdRT}, \qquad (3)$$

where σ - is the surface tension; d - the density of the liquid; r - the radius of curvature; M - the molecular weight; R - the universal constant; and T - the absolute temperature. It is evident that liquids which wet the capillary, as a result of the large curvature of the concave surface, have a considerably lower vapor pressure in the capillary than in wide tubes. Nevertheless evaporation is incomparably quicker, since the free surface of the liquids increases relatively, to a considerably greater extent than the vapor pressure decreases. E.g., the free surface of a liquid contained in a capillary of diameter 0.6 mm amounts to about 0.6 mm^2 and not 0.3 mm^2 as for a flat surface of the same diameter, while the

1) See plate, p. 431.

vapor tension above the meniscus with the corresponding curvature is lowered 5%. In addition the solution in a capillary is under considerably better conditions for heat transfer.

In order to decrease the evaporation velocity from capillaries when using an ultramicro method the work is carried out in a humid atmosphere. Aqueous solutions of salts which have a lower vapor tension than water evaporate under similar conditions somewhat slower than water, but not to such an extent that it excludes the necessity of working in a humid atmosphere. The volume of saturated salt solutions contained in capillaries increases rapidly when working in a humid atmosphere as a result of an evening out of the vapor pressure in the system vapor above pure water (humid atmosphere) – vapor above the saturated solution in the capillary. The hygroscopicity of the dissolved salt is also of significance. Saturated solutions of salts should not therefore be handled in a humid atmosphere. The figures given in Table 3 confirm what has just been said.

TABLE 3

Substance	Diameter of capillary in mm	Volume of solution in mm^3	% Change in volume in min. to total volume	
			Ordinary Atmosphere	Humid Atmosphere
Water	0.12	0.02	-1.0	-0.1
1 M Potassium nitrate	0.12	0.02	-0.4	-0.06
Saturated calcium chloride solution	0.12	0.02	+0.02	+0.6

Organic liquids which have to be used for the preparation of solutions, or for extractions, evaporate particularly rapidly as a result of their low heat of vaporization or their high vapor pressure. Such compounds as ether and chloroform, which have particularly high vapor pressures, are ejected from thin capillaries with one end sealed by the action of their own vapors forming a rapidly evaporating drop at the open end of the capillary. The evaporation of organic liquids can be cut down by working in an atmosphere of the vapor of the respective liquid.

The increase in the surface of a liquid relative to its volume has its own consequences, in addition to an increase in adsorption of the substance from solution by the walls of the tube and of an increase in evaporation rate, the surface tension also increases and attains a considerable value when working with capillaries. This fact is of major importance in developing the experimental technique of ultramicro methods. On one hand the position is complicated by the necessity of overcoming surface tension in transferring liquid from capillary to capillary, while on the other hand this fact excludes the possibility of loss of solution by spilling; and also, as a result of the stable (within the limits of evaporation velocity) position of the meniscus, it enables the amount of solution to be measured accurately. The cleanliness of the surface of the liquid plays an important part in working with capillaries. The presence of surface active agents in the solution increases the wettability of the glass surface by the solution and leads to experimental errors. Solutions of salts have a higher surface tension than water, the surface tension increasing approximately in proportion to the number of equivalents of dissolved salt. This increase in surface tension explains the creeping of salts (e.g., NH_4Cl), which is a serious handicap when working with capillaries. The creeping of precipitates along the glass also interferes with work (e.g., the precipitate of nickel dimethylglyoxime). As a result of the increase in surface tension the evolution of gas from solutions contained in capillaries occurs in a totally different way from that in macro methods; a bubble of gas which has been formed often does not reach the surface of the liquid but remains where it has been

formed and with time assumes greater proportions and finally divides the solution into two isolated parts. The horizontal position of the capillaries help the surface tension to give rise to this state of affairs. Heating the liquid to boiling, which is characterized by the appearance of bubbles of vapor under the liquid level, followed by subsequent evolution, is excluded in ultramicro methods in contrast to macro methods, since together with intensive vapor formation, the surface tension decreases with increasing temperature, with the overall result that the liquid is expelled from the capillary particularly easily.

All the same the ultramicroscopic methods still have great advantages. By enabling small amounts of material to be determined, the method, at the same time, in a number of cases gives an increased sensitivity as compared with the macro methods. This can be illustrated by considering the detection of an element in the form of one of its compounds.

The sensitivity of a reaction is characterized by two mutually related quantities; the limit of identification and the minimum concentration. The limit of identification is the smallest amount of a substance which can still be detected by a given reagent under the definite experimental conditions used for examining the reaction products. The minimum concentration shows at what dilution of the test solution a reaction still gives positive results under certain experimental conditions. It is expressed by the ratio of unit weight of material detected in solution to the weight or volume of solvent. Knowing the volume in which the reaction has been carried out, it is possible to calculate the minimum concentration from the limit of identification and vice versa by the relations:

$$C_{min.} = 1 : \frac{V}{m}, \quad m = C_{min.} \cdot V, \qquad (4)$$

where $\underline{m}$ is the limit of identification in g; $\underline{V}$ is the volume of solution in ml; $C_{min.}$ - the minimum concentration.

By varying the experimental conditions it is possible to increase the sensitivity of a given determination.

The intensity of the color of a solution depends on the presence of a corresponding amount of a colored substance in the path of the rays of light. The nature of a colored substance is characterized by the value of its extinction coefficient. The sensitivity of a color reaction indicates the least amount of a colored substance located in the path of the light necessary to give an observable color to the solution. If it is assumed that the Lambert-Beer laws E = KCl still holds at very low concentrations of substance, then one can talk of a minimum concentration for a definite reaction only for a layer of a given thickness, so that the concept of "minimum concentration" acquires a definite meaning. For a given colored substance (K = constant) and defined conditions of observation, the product Cl = E is a constant, from which it follows that the value of the minimum concentration is determined by the nature of the colored substance and the selected length of the path of light; it does not depend on any other parameter, not even on the cross section of the column of liquid through which the light passes. The sensitivity of a reaction is determined by the limit of identification as well as by the minimum concentration

$$m = C_{min.} \cdot V, \qquad (4)$$

But $V = \underline{l} \cdot S$ where $\underline{l}$ is the selected thickness of the layer of solution (the length of the path of light); $\underline{S}$ - the cross section of a column of solution from which $\underline{m} = C_{min.} \cdot \underline{l} \cdot S$, i.e., the limit of identification is proportional to the cross section of the solution.

For the observation of color in the ultramicroscopic method coloriscopic capillaries are used in which the thickness of the layer of the colored solution

is commensurable with that in a macro method, but the section is considerably smaller so that the limit of identification can be essentially increased. The section of a column of the solution in the ultramicro method is usually 10^4 times smaller than in a macro method. The same ratio therefore holds for the limits of identification in the two respective methods. The minimum concentration which is independent of the cross-section of the solution for commensurable thicknesses, being related to unit length, is equal for both the macro and ultramicro methods. Nevertheless if columns of solution of different cross-sections are used for observation the Lambert-Beer law is not followed, as a result of some physiological peculiarities of the eye; thus if two columns of different cross-sections but containing colored solutions of the same concentration are examined under similar conditions, it appears that the one with the larger cross-section is colored more intensely than the other. It is possible therefore for a color which is unobservable in a column of lesser cross-section to be observed by the eye in a column with a greater cross-section.

This is particularly marked in ultramicroscopic determinations and is bound up with the use of capillaries the diameters of which may differ among themselves by 2, 3, 4 or more times.

Such are the general features, principal characteristics , drawbacks, and merits of the ultramicroscopic chemical method of analysis, which is opening up new possibilities for chemists to investigate the composition of substances.

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SPECTROPHOTOMETRY IN CHEMICAL ANALYSIS

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Spectrophotometry has found a very wide application in chemical research including the solution of a number of analytical problems. By means of spectrophotometry the structure of a number of organic and inorganic compounds has been studied, and a number of analytical methods for both organic and inorganic compounds developed. Nevertheless, until recently the development of the spectrophotometric method of analysis has been hindered by the absence of the requisite apparatus. With the appearance of the Russian spectrophotometer, the SF, wide possibilities have been opened up for chemists of using this apparatus in the various branches of chemistry: for the study of the composition of complex compounds, organic compounds, and for the analysis of various substances, mainly in the presence of several components. By means of a spectrophotometer it is possible in a number of cases, to establish in addition the quantitative relationships of different valency states of the same element in solution. E.g., it is possible to determine the amounts of vanadium (V) and vanadium (IV), present in solution also containing chromium (III) and chromium (IV), etc..

Spectrophotometry widens the field of application of organic reagents in the analysis of inorganic compounds, since it enables several colored compounds to be determined in one solution.

The advantages of the spectrophotometric method of analysis as compared to other photometric methods are the possibilities of analyzing multicomponent systems. In addition, the sensitivity of the determination is increased, since the measurement is carried out at wave lengths which correspond to maximum absorption. The accuracy of the determination also increases, particularly when the apparatus is fitted for photoelectric registration. The SF is of this type.

Even greater possibilities are opened up for analytical chemists if absorption spectra in the ultraviolet and infra red are used, because thereby colorless compounds can be determined. The SF enables work to be carried out in the ultraviolet region by using a hydrogen lamp as the light source. In the ultraviolet region as many as 4 components can be determined quantitatively when present together.

In the present article the authors do not intend to give a complete picture of the spectrophotometric work; their idea is to show by means of a number of examples the various problems solved by means of spectophotometry and also to demonstrate its advantages by actual experimental data.

Qualitative and Quantitative Methods of Analysis by Means of Absorption Spectra

Qualitative analysis by means of absorption spectra is based on a comparison of the spectrum of an unknown solution with the absorption spectra of a solution containing known components.

It is evident that in order to carry out qualitative analysis it is necessary to have a selection of absorption curves for the group of substances being analyzed which have been either obtained experimentally in the laboratory or from literature sources. In general for the qualitative analysis of solutions of inorganic compounds

for which no preliminary results are available, turning to the absorption spectra is hardly reasonable because of the considerable dependence of these on a multitude of factors.

Quantitative methods of spectrophotometric analysis are based on the Lambert-Beer absorption law. A detailed exposition of this law is given in a number of textbooks [1, 2, 3, 4, 5].

The Beer law is only applicable for cases where the absorption coefficient is independent of concentration. However, such an independence of the absorption coefficient and consequently of the absorption spectra is only obtained for small concentration changes. The range of concentrations within which a solution obeys the Beer law is determined experimentally in each individual case.

Deviations from the Beer law can arise from a number of causes: the dissociation of colored complexes in dilute solution [6]; the change of state of intermolecular dissociation for changes in the pH [7]; displacement of the absorption maximum with concentration changes, and in some cases as a result of the formation of new complexes [2].

The determination of the concentration of one-component systems is carried out on the basis of the Lambert-Beer law, from which it follows that $c = D/K$, where K is the extinction coefficient determined by measuring the optical density of a solution with a given concentration. In practice it is more usual to use a graphic relation between extinction coefficient and concentration. The most simple method is the method of additions, which is applied to the analysis of solutions for which there are existing guiding results on the concentration. In this case a known amount of the component being determined is added to the solution with unknown concentration c_x. The concentration required is then determined by the formula

$$c_x = c_a \frac{D_x}{D_{x+a} - D_x} = c_a \frac{\log T_x}{\log \frac{T_{x+a}}{T_x}},$$

where D_x and T_x are the optical density and the transmission of the solution with a known concentration, and D_{x+a} and T_{x+a} the optical density and transmission for the same solution after the addition of a known weight of the test material.

In recent years the differential method has found application. This method consists in measuring the extinction of the test solution with respect to a standard solution of the same compound but of know concentration [8].

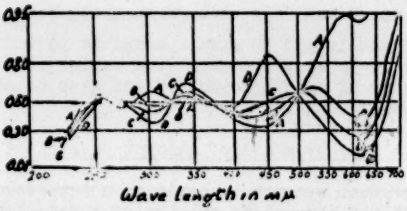

Fig. 1. Absorption curves for bromothymol blue at various pH's Solvent, water. A - pH 5.45; B - pH 6.95; C - pH 7.50; D - pH 11.60

In carrying out an analysis the choice of wave length to be used is very important. In general, measurements are made at those wave lengths which correspond to maximum absorption. Where the spectra consists of several maxima, the widest of the maxima should be chosen, because both the change in slit width of the spectrophotometer and the set up used for adjusting the wave lengths used will have the least effect. For solutions the absorption spectra of which are strongly dependent on the acid-

ity, it is convenient to use the point of intersection of the absorption curves for different pH's, e.g., the wave length of 501 mμ on Fig. 1 [9].

Determinations of the concentrations of a two-component solution are carried out at 2 wave lengths; in the case where they do not affect one another the following equations can be used

$$\begin{aligned} D_{\lambda_1} &= K_{a\lambda_1} c_a + K_{b\lambda_1} c_b \ , \\ D_{\lambda_2} &= K_{a\lambda_2} c_a + K_{b\lambda_2} c_b \ . \end{aligned} \qquad (1)$$

The coefficients $K_{a\lambda 1,2}$ and $K_{b\lambda 1,2}$ are determined by measuring the optical densities $D_{\lambda 1}$ and $D_{\lambda 2}$ of solutions of known concentrations.

The criteria for the selection of the wave lengths λ_1 and λ_2 are the two conditions:

1) The values D_{λ_1} and D_{λ_2} should lie within the range 0.3 to 1 (the transmissions respectively in the range 10 - 50%) [2].

2) The ratios $K_{a\lambda_1}/K_{b\lambda_1}$ and $K_{b\lambda_2}/K_{a\lambda_2}$, i.e., the ratios of the absorption coefficients of the two components should be a maximum [9].

When measurements are made at wave lengths satisfying the given conditions the relative error $\Delta c/c$ will be a minimum.

In special cases the analysis can be simplified considerably.

Thus, if there is a part of the absorption spectra where only one of the components is absorbed, then the concentration can be determined by the relations

$$c_a = \frac{D_{\lambda_2}}{K_{a\lambda_2}} \qquad c_b = \frac{K_{a\lambda_1} D_{\lambda_2} - K_{a\lambda_2} D_{\lambda_1}}{K_{a\lambda_2} K_{b\lambda_1}}$$

If there is such a part for each component, then the analysis can be carried out independently by the equations:

$$D_{\lambda_1} = K_{a\lambda_1} c_a \ , \quad D_{\lambda_2} = K_{b\lambda_2} c_b \ .$$

The quantitative analysis of solutions containing components which mutually affect each other is carried out by means of an empirical graph which expresses the relation between the optical density and the various concentrations of the two components, or by removing the influence of one of these components by changing the pH or the valency, and also by binding it as a complex.

A Description of the SF-11 Spectrophotometer

The non-registering photoelectric quartz spectrophotometer SF-11 is designed for the determination of optical densities in the wave length range from 2,200-11,000 A.

The optical set up of the spectrophotometer is shown schematically in Fig. 2.

Light from a source 1 [incandescent lamp (glower) for visible light and a hydrogen lamp for the ultraviolet] is focussed by a condensing mirror 2 on to the entrance slit 4.

The divergent light beam which passes throught the slit is converted by the concave mirror 5 into a parallel beam and reflected on to prism 6, one surface of which is coated with aluminum. The divergent light reflected by the prism is focussed by mirror 5 on to the slit 4 which is the exit slit of the monochromator. After passing throught the cell 7 containing the test solution, the part of the spectra chopped off by the slit 4 falls on the photoelement 8.

The linear dispersion of the spectrophotometer in the region 8000 - 4000 A increases from 65 to 10 mμ/mm. Thus the chopped off part of the continuous spectra for a slit width less than 0.1 mm does not exceed 6.5 mμ/mm.

Since the half width of the absorption band for solutions of inorganic compounds in the majority of cases amounts to 100 - 150 mμ, the light flow passing through the solution can be regarded as monochromatic.

The external appearance of the SF-11 is shown in Fig. 3.[1)]

The operating procedure for the SF-11 is very simple. Measurement of the whole absorption spectra in the 400 - 1000 mμ range at intervals of 20 - 25 mμ only takes 10 - 15 minutes, while three measurements of the optical density at the selected wave length takes 2 - 3 minutes.

The apparatus gives completely satisfactory reproducibility-deviations in repeated measurements do not exceed 0.8 - 1% - while the mean deviation only amounts to 0.4 - 0.5%. For errors obtained with different spectrophotometers see [10].

Apart from spectrophotometers other apparatus [83, 84, 85] are used for the analysis of two and three components by means of their absorption spectra.

The Use of Spectrophotometry in Chemistry

Spectrophotometric methods are widely used in all branches of chemistry. A large amount of work on the structure of organic compounds has been published by Soviet scientists. Thus the absorption spectra of several intermediate products and azo-dyes of the naphthalene series [11] and a number of derivatives of di- and tri-phenylmethane have been studied, whereby a number of important conclusions could be made as to their structure [12]. The absorption spectra of benzene derivatives [13, 14], heterocyclic compounds of rhodamine and N-phenylrhodamine [15], and of phenylhydrazine derivatives have been studied.

A number of papers by Soviet scientists has been devoted to the spectrophotometric investigation of biuret complexes, enabling an approach to be made to protein structure [17, 18, 19, 20]. Several research workers have used the spectrophotometer for the determination of the pH of solutions [21, 22] by means of calibration curves $D = f(pH)$.

The spectrophotometric method in the red part of the spectrum has also been used for selecting the ratios of standard solutions of cobalt chloride and ferric chloride in order to imitate the color of Bogen's indicator [23]. A lot of work has been devoted to the study of the composition of complex compounds by means of the spectrophotometer, e.g., the absorption spectra of cobalto-(II)-halide complexes in various organic solvents: in ethyl, butyl, and propyl alcohol and in acetone have been studied. It was shown that the complexes $CoCl_4^{2-}$ and $CoBr_4^{2-}$ [24] exist in acetone. Complexes of copper (II) with sulfosalicylic acid have also been examined with the spectrophotometer. It was shown that pH affects the absorption spectra of similar complexes [25]. It was established that complexes CuR or CuR_2^{2-} could exist either independently or together in solution according to the pH [26].

The interaction of halogens dissolved in carbon tetrachloride [27] has been examined, and a number of other investigations carried out.

A Short Review of Spectrophotometric Methods of Analysis

For analytical chemists it is the application of the spectrophotometric method to the analysis of organic and inorganic compounds which is of the greatest interest. There are hundreds of papers on this topic. In this short review therefore we shall confine ourselves to the most typical examples of the application of this method, analysis of organic compounds being only touched on very briefly.

1) See plate p. 431.

Analysis of Organic Compounds

A spectrophotometric method has been developed for the determination of m-nitrobenzene and trinitrotoluene by treating them with alkali in acetone solution [28]. A quantitative method has also been proposed for the determination of azotols and aromatic diazo compounds. The absorption spectra of these compounds have been studied with the help of a photoelectric-spectrophotometer in the wave length range 220-1000 mμ in the near ultraviolet [29]. Spectrophotometric methods have been proposed for the determination of acetaldehyde in blood [30], for the determination of formaldehyde and furfurol when present together (by the absorption of a colored compound with Schiff's compound)[31], for diacetyl (by the absorption of a colored compound obtained by interaction with chromotropic acid in sulfuric acid at 570 mμ) [32], for phthalic acid (by measuring absorption in the ultraviolet region at 276 mμ) [33], for 8-hydroxyquinoline and its products (by absorption of their complexes with Fe^{3+} at 650 mμ [34], for anthracene [35], typtophane [36], nicotine (by absorption in the ultraviolet region at 260 mμ [37],and for a number of other compounds.

Analysis of Inorganic Compounds

Spectrophotometric methods have been worked out for the determination of a number of elements and inorganic compounds. In this review it is impossible to include even a significant amount of the work which has been devoted to this question in recent years. We shall therefore confine ourselves to a few typical examples of the determination of one, two and three components in solution.

The Determination of One Component

Copper. Copper has been determined spectrophotometrically by measuring the absorption of the complex formed between Cu (II) and rubeanic acid [38] or the absorption of thecomplex formed between Cu (II) and benzoinoxime at 440 mμ after extraction with chloroform. Copper has been determined by the latter method in iron alloys with a mean error of 0.005%. Ni and Co interfere [39].

Iron. Iron has been determined in iron ores containing up to 58% Fe by measuring the absorption of the complex formed between Fe^{3+} and 5-hydroxy-3-(hydroxymethyl)-1,4-pyppone from solutions with pH 6.3 - 6.5 at 440 mμ.

The optimum concentration is 0.0001 - 0.0005 mg Fe/ml. The accuracy of the method is 0.05%, despite the high dilution of the test solution [40]

Iron has also been determined in high melting alloys by measuring the maximum absorption of the complex between Fe^{2+} and 1-10 phenanthroline at 490 mμ [41].

Aluminum. For the spectrophotometric determination of aluminum in steels the complex of aluminum with hydroxyquinoline extracted in chloroform has been used. A colorimetric variation of the method was proposed by Mervel [43] and worked out by Kuskova for the determination of aluminum in steels [44]. The absorption of the chloroform solution of the complex was measured at 390 mμ. The accuracy of the method is ca. 5% for an Al content of 0.005 - 0.1% [45].

Beryllium. A spectrophotometric method has been proposed for the determination of small amounts of beryllium (0.0015 - 0.23%) in aluminum, based on the measurement of the absorption of the complex formed between beryllium and sulfosalicylic acid $[Be(C_6H_3SO_3OCO_2)_2]^{4-}$ at 317 mμ. Interference from Al is removed by combining the Al with ethylenediaminetetracetic acid or its salts. Fe and Cu interfere [42].

Lead. Lead has been determined in copper by means of the absorption of its complex with dithizone [46]. Dithizone has also been used for the spectrophotometric determination of other metals [47].

Nickel. For the determination of Ni the absorption of its complex with 1,2-cycloheptanedionedioxime (heptoxime) has been used.

The absorption curve has 2 maxima, the position of which depend on the pH of the solution and the time from the moment of inception of the reaction. This reagent has been shown to have no advantages over dimethylglyoxime [48]. A similar method has been proposed for the determination of Ni in which the absorption of the complex of Ni with nioxime (1,2-cyclohexanedionedioxime) was measured [49].

Cobalt. As an example of the spectrophotometric determination of cobalt, its determination in atmospheric dust by measurement of the absorption of its complex with nitroso-R-salt [50] may be quoted. This complex was suggested by Malyuga for the colorimetric determination of cobalt [51].

Vanadium. For the determination of vanadium in iron alloys the absorption of the phosphovanadotungstate complex first suggested by A.P.Vinogradov for the colorimetric determination of V [52] has been used. The maximum absorption of the complex is at 365 mμ; for analysis however it is more convenient to take measurements at 480 mμ [53].

It has been suggested that vanadium can be determined by measurement of the absorption of its complex salt with hydrogen peroxide in the ultraviolet at 290 mμ. For measurements in the ultraviolet the Beer law is obeyed for solutions with concentrations of from 0 to 0.125 mg/ml V. Ti and $Cr_2O_7^{2-}$ interfere to a lesser degree than when the measurements are made in the visible spectrum [54].

Molybdenum. Molybdenum in steel has been determined by the measurement of the absorption of the complex between molybdate and phenylhydrazine in acid solution at 565 mμ. 0.002-0.010 mg Mo can be determined with an accuracy of 2.9% relative units [55].

Chromium. For the micro determination of Cr in skin the absorption of the reaction product between chromate and diphenylcarbazone at ca. 530 mμ[1] has been measured [56].

Tellurium. Tellurium has been determined by measuring the absorption of the iodotellurate complex at 335 mμ, although this complex has an even greater maximum at 285 mμ. The Beer law however is only obeyed at 335 mμ, and then only within narrow concentration limits 0.2-2 μg Te/ml [57]

Rare Earth Metals. The possibility of spectrophotometric determination of the rare earth elements is of special interest because the methods of analysis for this group are very limited (usually X-ray spectrographic analysis is used). An investigation of the absorption spectra of solutions of chlorides, sulfates, nitrates, perchlorates and acetates of 11 rare earth elements in the wave length region 220 - 1000 mμ showed that the absorption spectra of the different salts of the same elements were almost identical. Some displacement of the spectra were observed for neodymium, samarium, europium, and gadolinium in solutions of their acetates. For analytical purposes it is more convenient to use the wave lengths adduced in Table 1 for each of the rare earth elements in the presence of other elements of this group since in this wave length interval Sc, Y, La, and Th do not absorb and the others do not interfere so much.

Mention may be made here of an indirect method for the determination of calcium in blood by measuring the excess Ce (IV) which has to be added to oxidize the oxalate combined with the calcium. The absorption of Ce (IV) was measured at 315 or 390 mμ. The mean error is ±2.2% [59].

TABLE 1

Element	λ in Å	Element	λ in Å
Pr	4445	Gd	2728
Nd	5218	Er	3792
Sm	4020	Tu	6825
Eu	3939	Yb	9750

1) Measurements were made on a Pulfrich photometer.

Elements of the Platinum Group

A number of spectrophotometric methods have been proposed for the quantitative determination of elements of ths platinum group.

It has been proposed that platinum can be determined by means of the absorption of the yellow color of the solution obtained by the interaction of $PtCl_4$ and $SnCl_2$. Aqueous solution were measured at 400 - 300 mμ. Solutions in amyl acetate have also been measured, but they are less stable. The differential method of measuring the absorption was used. The accuracy of the method is completely satisfactory [8]

A method has been proposed for the determination of ruthenium as potassium ruthenate in 2 M KOH solution [60]. The absorption spectra of potassium ruthenate has a maximum at 465 mμ. The Beer law is obeyed if the ruthenium content is within the limits $1 \cdot 10^{-4}$ - $4 \cdot 10^{-4}$ M. Pt, Ir, Pd and Rh do not interfere since they do not exhibit an appreciable absorption at 400 mμ. In addition they do not fuse easily with alkali (an operation necessary to get the ruthenium into solution).

For the spectrophotometric determination of osmium, measurements of the absorption of the rose-red colored complex of osmium (VIII) with thiourea in acid solution has been adopted [61]. The maximum absorption of this complex is at 480 mμ, nevertheless it is recommended that quantitative determinations of osmium should be carried out at 540 mμ, since palladium does not interfere at this wave length.

A spectrophotometric method has also been developed for the determination of rhodium (III) with sodium hypochlorite at a pH of 4.7-7.2 [62]. Maximum absorption occurs at 665 mμ; Pd, Pt, Au, Fe, Cr and Ni do not interfere even for considerable amounts of them, while Ru, Os, Ir, Co, Mn and Cu do not interfere if their contents are low compared to that of rhodium. Only iodides and iodates of the common anions interfere. It is best to determine rhodium in amounts of $5 \cdot 10^{-4}$ - $2 \cdot 10^{-3}$%. The experimental error is ~0.6% relative units.

Phosphorus. Phosphorus has been determined spectrophotometrically after formation of phosphomolybdic acid $H_3[P(Mo_3O_{10})_4]$ in sulfuric acid at a pH of ca. 1. The absorption of this acid is measured at 380, 400 and 420 mμ. Si and Fe interfere [63].

Silicon. For the determination of silicon in vanadium and uranium the absorption of the silicomolybdic complex is measured at 390 mμ after separation of metals with cupferron. The Beer law is obeyed for Si contents of 0.02 - 0.28 mg/100 ml. The reproducibility is ±0.004 mg Si [81].

Nitrates. Nitrates have been spectrophotometrically determined in galvanized silver baths for amounts of nitrate of 0 - 120 g/liter. The maximum absorption of KNO_3 was measured in the ultraviolet at 302.5 mμ. The maximum is displaced slightly with change in concentration of NO_3^-. The accuracy of the method is ±2% relative units [64].

Flurine. It has been proposed that fluorine in sea water be determined by measuring the absorption at 512 mμ of solutions containing the indicator zirconalizarin-sulfonate and adjusted to pH 4. The fluorine content is determined by the decrease in absorption of the indicator. Borates, Fe, PO_4^{2-} do not interfere. [65].

Iodine. Spectrophotometric determination of iodine in rocks, soils and other natural objects has been carried out by measurement of the absorption of the reaction products of iodine with starch at 575 mμ in sulfuric acid solution. The iodine is initially oxidized by $KMnO_4$ to IO_3^-, which then reacts in sulfuric acid solution with KI in the presence of starch to liberate iodine. The mean error is 0.9%, maximum error 2.5% [66].

Hydrogen Sulfide. As an example of the determination of a gas spectrophotometrically, we quote the method developed for H_2S which is based on the absorption of H_2S in a solution of zincate to form ZnS which is then reacted with an acid

solution of p-aminodimethylaniline with the addition of $FeCl_3$. The absorption of the methylene blue formed is measured at 670 or 750 mμ. The accuracy of the method is about ±3.0% for a H_2S content of 0.1 - 0.2 mg H_2S [67].

The Determination of Two Components

One of the first to use the spectrophotometer for the analysis of mixtures containing two colored components was Uspensky [68]. Babko and Korsun [87] have considered in detail the conditions for colorimetric determination in mixtures of two colored compounds. Komar [88] has proposed simple methods for calculating the equilibrium constant and the molecular absorption coefficients of most colored complex compounds used in spectrophotometric analysis, and also proposed methods for the spectrophotometric analysis of mixtures of compounds which do not obey Beer's law.

Below we have adduced a few examples of the spectrophotometric determination of two components in various industrial products.

Chromium and Manganese. Maltsev and Davydov [69] have worked out a spectrophotometric determination of chromium and manganese in steels and ferro-alloys based on the oxidation of Cr and Mn respectively to $K_2Cr_2O_7$ and $KMnO_4$. The maximum absorption of $K_2Cr_2O_7$ is located at 430 - 450 mμ while that of $KMnO_4$ is at 510 - 550 mμ. $KMnO_4$ can be determined directly at 530 mμ, since the absorption of $K_2Cr_2O_7$ at 530 mμ is negligible; but in the case of $K_2Cr_2O_7$, it is necessary to apply a correction to its absorption because at 450 mμ $KMnO_4$ exhibits some absorption. This method was subsequently used by other investigators [70, 71][1].

Bichromate and Chromate. A method has also been proposed for the spectrophotometric determination of $K_2Cr_2O_7$ in solutions saturated with respect to $K_2Cr_2O_7$ and K_2CrO_4. The absorption is measured at 425-500 mμ for which there is a difference in absorption for CrO_4^{2-} and $Cr_2O_7^{2-}$. A calibration curve is constructed at 528 mμ [72] for the absorption of mixtures of CrO_4^{2-} and $Cr_2O_7^{2-}$ for various ratios of these ions and at a constant chromium content.

Iron and Titanium. These two elements have been determined in cathodic nickel. Tyron (Na_2-1,2-dihydroxybenzene-3,5-bisulfonate) was the reagent used. The absorption of the iron complex was measured at 560 mμ and that of the titanium complex at 399 mμ after destruction of the iron complex by means of $Na_2S_2O_4$. The accuracy of the method is reasonably good [73].

Titanium and Vanadium. Babko and Volkova have carried out a detailed investigation of the titanium and vanadium complexes of hydrogen peroxide with a Pulfrich photometer. They have proposed a photometric determination of these elements in their mixtures.

Iron and Aluminum. A spectrophotometric method has also been worked out for Fe and Al based on the measurement of the absorption of their complexes with ferron. The absorption of the iron complex was measured at 600 mμ while that of the aluminum complex was measured at 370 mμ [74].

Molybdenum and Niobium. Mo and Nb have also been determined spectrophotometrically when present together. Mo is colored with thiocyanate and Nb with H_2O_2. [75].

Determination of Three Components

There are a number of papers on the spectrophotometric determination of three component mixtures, but the accuracy hitherto obtained is not very high.

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1) Babko and Korsun demonstrated the possibility of determining $K_2Cr_2O_7$ and $KMnO_4$ in their mixtures by means of a Dubosq colorimeter in conjunction with selected filters.

Titanium, Vanadium, and Molybdenum. For the determination of titanium, molybdenum and vanadium when present together the absorption of the complexes formed between these elements and H_2O_2 in perchloric at 410 mμ (Ti), 460 mμ (V) and 330 mμ (Mo) was determined. However as the author points out this method does not pretend to be a substitute for other methods of determining V and Mo [76].

Cobalt, Copper, and Iron. A method has been developed for the determination of these three elements when present together as thiocyanates extracted in acetone [77]. The thiocyanate complex of Co (II) has a maximum absorption at 625 mμ, that of Cu at 380 mμ and that of Fe (III) at 480 mμ. Since the color of the Cu thiocyanate complex is very unstable it is proposed that a small amount of oxidizing agent be added to stabilize it in solution. Methods are also adduced for eliminating the effects of some other cations and anions.

The accuracy of the determination of these elements is low. For a content of Co and Cu >50 mg and of iron >5 mg the accuracy is ca. 10% relative units.

The number of elements determined spectrophotometrically increases continuosly. It is impossible in this brief review to enumerate all the applications of the spectrophotometer; nevertheless from what has been said it is possible to get an idea of the potentialities of the method, particularly for the determination of three components in solution.

EXPERIMENTAL

It was our intention in this investigation to develop a spectrophotometric method for the determination of vanadium and titanium when present together, using the yellow color of ammonium vanadate in sulfuric acid solution, and the blue color of vanadium (IV) solution in sulfuric acid for the determination of vanadium, and the color of the complex formed between titanium and chromotropic acid for titanium. We therefore studied the absorption spectra of the solutions indicated and the effect of a number of factors on the absorption.

It should be noted that the absorption spectra of vanadium (III) and (IV) have been studied in solutions of perchloric and hydrochloric acids respectively for constant ionic strengths of the solution. Basically, however, this investigation was devoted to the absorption spectra of vanadium (III) in order to establish the nature of the hydrolysis product of vanadium (III) - (VOH^{2+}) [78].

All measurements were made on the SF-11 photoelectric spectrophotometer using cells with a 1 cm layer thickness.

Fig. 2. Optical diagram of spectrophotometer SF-11.

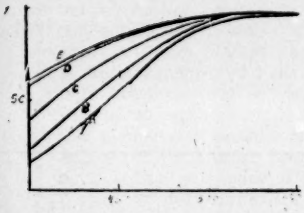

Fig. 4. Transmission curves of NH_4VO_3 for various vanadium concentrations. All solutions were 0.8 N with respect to H_2SO_4. A) 4 mg V. B) 3 mg, C) 2 mg and D) E-1 mg V per ml.

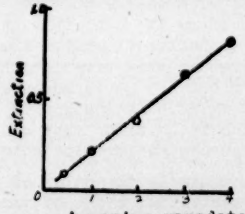

Fig. 5. Curve relating extinction to ammonium vanadate concentration; λ = 400 mμ.

Ammonium metavandate in 0.8 N H_2SO_4 was used as the original substance for the vanadium (V) and (IV) solutions. Contemporary theory of the structure of vanadium (V) compounds in acid media represent vanadium (V) in the form of a complex cation, which determines the bright yellow color of its solutions [79] Solutions of vanadium (IV) of a blue color are obtained by reduction of NH_4VO_3 by means of sodium sulfite or lactic acid with heating. For the color reactions of V (IV) vide [80]. Chromotropic acid, proposed by Tananaev and Panchenko for the qualitative determination of Ti and subsequently used for the quantitative determination of Ti in steel and cast iron [81], was used as the reagent for Ti. The titanium sulfate solution was prepared by treating $K_2TiF_2 \cdot H_2O$ with concentrated H_2SO_4, with subsequent solution of the titanium sulfate in 5% H_2SO_4.

Chromotropic acid was used in the form of a 6% aqueous solution. A few small crystals of Na_2SO_3 were added to improve the stability of the chromotropic acid solution.

Absorption Spectra of Vanadium (V) and (IV)

In order to determine the transmission spectra of vanadium (V), solutions of ammonium metavanadate with varying contents of V in 0.8 N H_2SO_4 were prepared. The transmission spectra of these solutions in the wave length ranges 400 - 1000 mμ and 300 - 1000 mμ are adduced in Fig. 4. These curves show that vanadium (V) has a maximum absorption in the visible spectrum at 335 mμ.

The form of the curves (Fig. 4) is independent of the vanadium concentration. On addition to the vanadium (V) solution of a small amount of titanium as the sulfate no significant change in the value of the vanadium transmission was observed through the whole wave length range studied (Curve D, Fig. 4). In order to check the validity of Beer's law for vanadium (V) a series of solutions was prepared with concentrations of vanadium ranging from 0 - 4 mg/ml in 0.8 N H_2SO_4. The extinction and vanadium concentration is illustrated in Fig. 5.

It is evident from Fig. 5 that a straight line is obtained for the concentration range 0.4 - 4 mg/ml V; all the experimental points lie very close to this line. For a layer thickness of 1 cm, 0.04 mg V/ml is the limiting sensitivity of this spectrophotometric determination of vanadium (V). A study of the effect of the acidity on the extinction of vanadium (V) at 500 mμ showed that changes in acidity from 0.4 N to 4 N H_2SO_4 has practically no effect on the extinction of the vanadium (V) solution.

It follows from these results that vanadium can be determined spectrophotometrically by the color of the vanadium (V) solution in sulfuric acid solutions from 0.4 to 4 N.

The transmission spectra of vanadium (IV) were taken in the wave length region 300 - 1000 mμ. The transmission spectra of solutions of vanadium (IV) in 0.8 N H_2SO_4 obtained by reduction of vanadium (V) with lactic acid on heating are given in Fig. 6, together with that of the lactic acid alone at the same concentration as that used with the vanadium solutions. From Fig. 6 it is evident that vanadium (IV) gives two transmission minima at 325 mμ and 750 mμ respectively. Similar transmission spectra are given by vanadium (IV) solution obtained by reduction of vanadium (V) with sodium sulfite. Curve D, Fig. 6 represents the transmission of lactic acid on its own; this has only one minimum at 330 mμ. For the determination of vanadium therefore the wave length of the second minima was used, i.e., the 750 mμ one. At this wave length the absorption of series of vanadium (IV) solutions in 0.8 N H_2SO_4 was measured; the concentration of the vanadium varied from 0.1 to 2 mg/ml. Extinction is plotted against vanadium concentration in Fig. 7, from which it is clear that all the experimental points lie on one straight line for the concentrations indicated.

Consequently the color of vanadium (IV) solutions follows Beer's law for a wide concentration range of vanadium. The sensitivity of the determination

of vanadium (IV) was found to be 0.01 mg V/ml for a layer thickness of 1 cm.

On investigating the effect of the acidity of the solution (with respect to H_2SO_4) on the estimation of vanadium, it was found that it has no effect over a wide range; nevertheless at low pH's (pH 2 - 3) the reduction of vanadium (V) to vanadium (IV) is not quantitative. Titanium does not affect the extinction of vanadium (IV) solution at 750 mμ. Neither does Fe^{3+} interfere, since it is reduced to Fe^{2+} by the sulfite. Thus vanadium can be determined spectrophotometrically by measuring the absorption of vanadium (IV) solutions. The determination of vanadium by the color of vanadium (IV) is more sensitive than by the yellow color of vanadium (V).

Absorption Spectra of the Complex Formed Between Titanium and Chromotropic Acid

In order to study the absorption of the Ti-chromotropic acid complex a solution of pH 2 was prepared containing 0.05 mg Ti [as $Ti(SO_4)_2$] and 0.5 ml chromotropic acid (6%) in 25 ml.

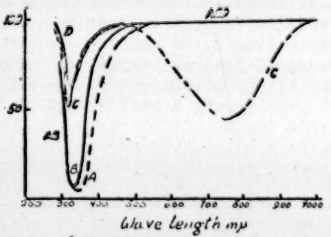

Fig. 6. Transmission curves for vanadium solutions (V), (IV); (V)+Ti (IV) and lactic acid.
A - NH_4VO_3+$Ti(SO_4)_2$ (0.4 mg V and Ti/ml; B - NH_4VO_3 (0.4 mg V/ml); C - VO^{2+}; D - lactic acid. All solutions in 0.8 N H_2SO_4.

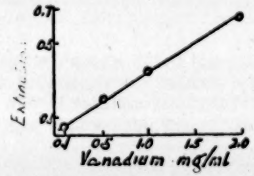

Fig. 7 Relation between extinction and vanadium (IV) concentration.

The adsorption of the solution was measured in the range 300 - 1000 mμ. In addition the adsorption spectra of a 6% chromotropic acid solution was taken (Fig.8).

Fig. 8 shows that the titanium-chromotropic acid complex has two transmission minima. The first is near the ultraviolet region at 350 mμ and belongs to the chromotropic acid (Curve A); the second at 475 mμ belongs to the complex. Determination of the transmission of the titanium complex should therefore be made at 475 mμ. If this value is compared with the wave length at which the transmission minimum of vanadium is obtained, i.e, 750 mμ, then it is clear that the determination of these elements when they are present together is comparatively simple. Subsequently measurements of the transmission of solutions of the titanium complex were made at different values of the acidity (with respect to H_2SO_4), Fig.9. From Fig. 9 it is clear that the acidity has considerable influence on the transmission of the complex; this is in agreement with Babko [86] and Generozov's results. The transmission increases considerably in going from 0.01 to 0.05 N H_2SO_4. In practice, therefore, in order to get the optimum color developed, the acidity of the titanium solutions should be adjusted to concentrations not greater than 0.01 N, since for lower acidities, changes in the transmission of the titanium complex do not occur. Therefore all further measurements were made with titanium solutions 0.01 N with respect to H_2SO_4.

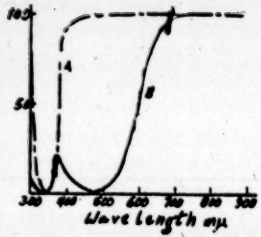

Fig. 8. Transmission curves for chromotropic acid and for the complex of titanium with chromotropic acid.
A - Chromotropic acid, B - complex of titanium and chromotropic acid.

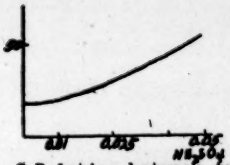

Fig. 9. Relation between transmission of the titanium-chromotropic acid complex and the acidity; λ = 475 mμ.

The effect of the amount of chromotropic acid was also investigated. On Fig. 10 the relation is given between transmission and chromotropic acid concentration for a constant amount of titanium (0.1 mg in 25 ml) at 475 mμ. This curve shows that the amount of chromotropic acid (within the range 0.5 - 2 ml) has very little effect on the transmission of the titanium complex). In all subsequent experiments therefore the amount of chromotropic acid added was kept at 0.5 ml.

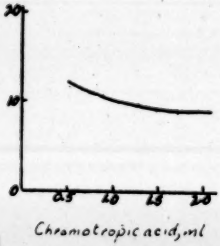

Fig. 10. Relation between transmission and amount of chromotropic acid.

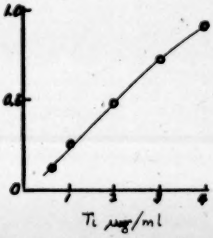

Fig. 11. Relation between the transmission of the complex formed between titanium and chromotropic acid and the acidity; λ = 475 mμ.

The color stability of the titanium complex was also investigated. It was found that even on long standing (48 hours) no change in the transmission of solutions of the complex occurred. A series of experiments was then carried out in which solutions were prepared with concentrations of titanium varying from 0.5 to 4 μg/ml in 0.01 N H_2SO_4 to which 0.5 ml of chromotropic acid solution was added. Extinction was measured at 475 mμ. The relation between extinction and titanium concentrations in solution is plotted in Fig. 11. All the experimental points lie on one straight line, which shows that the color of the titanium complex follows Beer's law.

Spectrophotometric Determination of Vanadium and Titanium When They Occur Together

In order to estimate the accuracy of the determination of vanadium and titanium when present together, solutions containing various ratios of the metals were prepared in 0.01 N H_2SO_4. One series of these solutions contained titanium sulfate and ammonium vanadate and their absorption was measured directly at 475 mμ after addition of 0.5 ml chromotropic acid and making up to a volume of 25 ml in order to determine the titanium.

In another series of solutions containing titanium sulfate and ammonium vanadate, a known excess of sulfuric acid was added before addition of the chromotropic acid; the whole was then adjusted with ammonia or NaOH to a pH of 2.

The third series of measurements was made after reduction of the vanadium by means of Na_2SO_3 or lactic acid. In order to do this a mixture of ammonium vanadate and titanium sulfate was made, the pH of the solution adjusted to 2, and a few small crystals of sodium sulfite or 1 ml lactic acid added. On heating for a few minutes the vanadium (V) is reduced to vanadium (IV). When this was done it was found that the solutions obtained were colored green and not blue, indicating an incomplete reduction of the vanadium (V) because of the low acidity of the solution. Actually on addition of a large excess of acid to the solution the reduction of vanadium (V) proceeds quantitatively. However, high acidity of the solution interferes with the development of the colored complex of titanium and chromotropic acid. We therefore adopted the following procedure after reduction of vanadium (V) in a solution whose acidity is high enough: the solution was transferred to a 10 ml standard flask and made up to the mark with distilled water. An aliquot of the solution was measured into a 25 ml flask, water added to bring the volume up to 20-23 ml, the pH adjusted to 2 by addition of ammonia and finally 0.5 ml chromotropic acid solution added and the volume made up to the mark. The absorption of this solution was measured at 475 mμ (for determination of the titanium) and at 750 mμ for the determination of vanadium). However, since at low concentrations of vanadium its determination in a cell with only a 1 cm layer is not sufficiently sensitive, it was determined by the absorption of the blue color formed before addition of the chromotropic acid at 750 mμ or by means of a cell with a greater layer thickness.

From Table 2 it is clear that for the determination of titanium in the presence of a large excess of vanadium (V) but without neutralization of excess acid the results are completely satisfactory even for low concentrations of titanium (Experiments 1 - 5). Mean error - 3% relative.

On introducing excess sulfuric acid with subsequent neutralization and adjustment of the pH to 2, the deviation of the titanium becomes considerable (20 - 30%) on the high side (Experiments 6 - 9), since in this case a color is superimposed which arises from the conversion of the vanadium (V) ion into a more complex ion. When titanium is determined with chromotropic acid in the presence of vanadium (IV) the results obtained are somewhat high, since the vanadium exhibits a certain amount of absorption at 475 mμ. The mean deviation is 5%. For more accurate measurements this factor must be taken into account.

In the case of vanadium satisfactory results can be obtained by measuring the absorption of vanadium (IV) solutions. The mean error in this case amounts to 5%.

As a result of this investigation the following analytical procedure is tentatively suggested for the determination of titanium and vanadium when present together; after separation of Ti and V as normally recommended [83], the solution containing both elements is made up to a known volume A. An aliquot is taken and diluted so that the normality of the acid used is ca. 0.01 N, when chromotropic acid is added and the solution made up to a standard volume B. The colored solution formed is then placed in the cell and its absorption at 475 mμ measured. From a calibration curve constructed beforehand the Ti content is then determined. When the solution is strongly acid it is reduced with Na_2SO_3 with heating, made up to a definite volume and aliquots taken. The pH of the aliquots is adjusted to 2 by

TABLE 2

Test No.	V taken, mg	Ti taken, mg	V found, mg	Ti found, mg	Difference, mg V	Difference, mg Ti	Error, % V	Error, % Ti	Observations
1	0.50	0.050	–	0.053	–	+0.003	–	+6.0	V introduced as NH_4NO_3, Ti as the sulfate, 0.01 N H_2SO_4. Chromotropic acid added and volume made up to 25 ml.
2	0.50	0.075	–	0.076	–	+0.001	–	+1.3	
3	0.25	0.050	–	0.052	–	+0.002	–	+4.0	
4	0.10	0.050	–	0.051	–	+0.001	–	+2.0	
5	0.75	0.090	–	0.092	–	+0.002	–	+2.3	
							Mean	3.12	
6	1.00	0.075	–	0.091	–	+0.016	–	+21.0	Conditions as above, but excess acid neutralized with NH_4OH.
7	1.00	0.075	–	0.086	–	+0.009	–	+12.0	
8	1.50	0.075	–	0.090	–	+0.015	–	+20.0	
9	1.00	0.250	–	0.250	–	–	–	–	In Experiments 10, 11, and 12, Ti and V are determined together after adjustment of the acidity to 0.01 N and addition of chromotropic acid.
10	2.50	1.000	2.30	1.000	-0.2	–	-8.0	–	
11	2.50	0.050	2.30	0.052	-0.2	+0.002	-8.0	+4.0	
12	1.50	0.025	12.50	0.023	–	-0.002	–	-8.0	
13	5.00	0.200	4.80	–	-0.2	–	-4.0	–	In Experiments 13, 14, and 15, Ti is determined in the mixture, V by the blue color.
14	5.00	0.100	4.80	–	-0.2	–	-4.0	–	
15	2.50	0.90	2.30	0.925	-0.2	+0.025	-8.0	+2.7	
16	2.50	0.90	–	0.937	–	+0.037	–	+4.11	Only Ti determined after reduction of V, neutralization of the solution and addition of chromotropic acid.
17	2.50	0.90	–	0.937	–	+0.037	–	+4.11	
						Mean	-5.3	±4.98	

means of NH_4OH and chromotropic acid added, the volume is then finally made up to a standard volume and the titanium determined at 475 mμ. Vanadium is determined in the solution obtained directly after reduction with Na_2SO_3 (i.e., before neutralization with NH_4OH, etc.), by measurement of its absorption at 750 mμ. The vanadium content is determined by means of a calibration curve constructed beforehand.

In conclusion we should like to express our thanks to A.P.Vinogradov, Corresponding Member of the Academy of Sciences, for his suggestion for compiling this report and for his interest in the work.

We also wish to thank G.I.Ostrozhenskaya, who kindly gave us the chromotropic acid.

SUMMARY

1. A short review is given of literature relating to use of the spectrophotometric method in various branches of chemistry during the last 4-5 years.

2. The absorption spectra of vanadium (V) and vanadium (IV) in acid solution and of the complex formed between titanium and chromotropic acid have been examined.

3. The effect of various factors (pH, amount of reagent, time of standing, etc.) on the value of the extinction of the complex of titanium and chromotropic acid, and also on the extinction of vanadium solutions, has been investigated.

4. A spectrophotometric method for the determination of vanadium and titanium when present together has been suggested. Vanadium is determined as vanadium (V) at 400 mμ or as vanadium (IV) at 750 mμ. Titanium is determined with chromotropic acid at 475 mμ in the presence of vanadium (IV).

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QUANTITATIVE X-RAY SPECTROGRAPHIC ANALYSIS

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Quantitative X-ray spectrographic analysis is based on a comparison of the intensity of the X-ray lines of the test sample and of a standard respectively, under identical, standard conditions, The intensity of these lines, all other conditions being equal, is proportional to the number of atoms of each element in the test sample. However, when a photographic method is employed for registering the spectra it is not the intensity of the lines but the corresponding blackening that is compared. The latter depends on the intensity in a non-linear manner, as a result of which many difficulties crop up in practical analytical X-ray spectroscopy. This non-linear relation is also the source of the largest analytical errors. One of the first attempts to overcome the difficulties encountered in X-ray spectrographic analysis arising out of this non-linearity between the intensity of a line and the corresponding blackening was made by Hevesy, who in conjunction with a number of his coworkers proposed a method conveniently called "the null method". This method consists essentially in adding to the test substance an amount of a standard element such that the blackening of the lines being compared becomes identical. This quantitative method of analysis became widely known and was included in all textbooks on X-ray spectrography [1, 2]. It was by means of this method that most of the early investigations in X-ray spectrographic analysis were carried out [3, 4, 5]. However, as the method came to be more and more widely used some of the fundamental drawbacks of Hevesy's method became evident, these drawbacks were connected with the necessity of repeating the analysis several times, and choosing the amount of standard element to be added to the test mixtures for equalizing the blackening of the lines being compared. This leads, apart from a considerable waste of time in production analysis, to an increase in the amount of substance necessary for analysis, and finally requires a large selection of standard elements. What has been said above shows that this method is not suitable for use under factory conditions, where the speed of analysis is nowadays of decisive importance. That is why investigators were often compelled with a corresponding sacrifice of accuracy to depart from strict observance of Hevesy and his successors recommendations and used for quantitative analysis lines with unequal blackening or separated from each other by distances in excess of the usually recommended 100 XU. Some authors when carrying out analysis in this way [6, 7] preferred to use a "blackening curve", experimentally constructed beforehand, others [8] carried out analysis by means of a series of calibration curves, implicitly including the relation between blackening and the intensity for a selected type of photographic material. In some special cases it is possible to carry out an analysis with sufficient accuracy on the assumption that the blackening of a line is, within narrow limits, proportional to the intensity.

Despite the apparent differences between the analytical methods mentioned above, which to various degrees enable them to be used for the solution of some particular practical problem, they all have a large number of coarse errors in common; firstly, the accuracy of these methods of analysis is less than the accuracy of Hevesy's "null method"; secondly they can only be used when the experimental conditions under which the fundamental calibration curve was obtained are very strictly controlled; such as strict standardization of the photographic

material, standard conditions of developing the spectrogram, the successful choice of exposure time during which the spectral lines under observation are located in the necessary blackening region, etc.. Non-observance even of only one of these factors immediately leads to a decrease in the accuracy of the analysis. Thus, although the drawbacks of the methods described are often worth the possibility of carrying out an analysis of a large number of elements rapidly, nevertheless the search for new analytical methods which ensure the necessary rapidity and accuracy of an analysis remains a practical problem.

During the last two years a number of investigations have been carried out which had as their aim the development and comparative testing of new methods of X-ray spectrographic analysis.

Some of the results of this work are given in the present article.

Use of the Form of the Spectral Lines for X-ray chemical analysis

It is known that [9] the form of a large group of X-ray lines of the elements remains practically unchanged when the atoms of these elements enter into the composition of chemical compounds, and does not depend on the aggregate state of the substance. Finally the form of the lines does not depend on their intensity. It was shown e.g., that the form of the $K\alpha_{1,2}$ line of elements, the atomic number of which is greater than or equal to 30, is closely described by the dispersion formula

$$I = \frac{I_0 \left(\frac{\Gamma}{2}\right)^2}{(\nu - \nu_0)^2 + \left(\frac{\Gamma}{2}\right)^2}, \qquad (1)$$

where I – is the intensity of a point on the contour of a line at a distance $(\nu - \nu_0)$ from the frequency corresponding to the maximum; I_0 – the maximum intensity of the line at the point $\nu = \nu_0$; while Γ – is a constant numerically equal to the width of the emission line at a height equal to half its intensity.

This means that if each point on the contour of the spectral line is characterized by a quantity n (either whole or fractional), which indicates how many times the intensity of the line at its maximum is greater than that at a given point on its contour, (i.e., making $n = I_0/I$), then a knowledge of the value of Γ will enable the width of the line at any section of it (x) to be calculated [9] accurately according to the formula (2)

$$x = \Gamma\sqrt{n - 1}. \qquad (2)$$

It is evident that the relation (2) will be valid for any given line independently of its intensity. Consequently it can be used [9] both for the direct study of the form of the X-ray emission line, and for the solution of the reverse problem, finding the value of n on the basis of given measurements of the width of the line at an arbitrary point on its contour and of the value of Γ.

By means of (2) it is possible to calculate the relative intensities of two or more lines (the form of which is described by a dispersion formula) if the values of Γ are known for each of them and the widths are measured at any arbitrary section, which is however the same for all the lines compared. In particular, if a point were found on the contour of one of the lines (considered as the standard line) the intensity of which were identical with the intensity of the peak of another line, located side by side with the first, the value of n, calculated for this point would be equal to the ratio of the intensities of these two lines. Thus, by measurements of the width of the lines of a series of standard elements and using formula (2) the basic problem of X-ray spectral analysis can be solved in a different way from those adopted previously. What has been said above is the basis

of the new method of quantitative X-ray spectrographic analysis. It can be carried out in practice by two methods. The first of these which is essentially completely analogous to Hevesy's "null method" was first proposed in 1937 [10] and as further tests have shown [11, 12, 13] can be used both in optical and X-ray spectroscopes. The second method was proposed and tested fairly recently [14].

Both methods are based on the fact that the true form of a line in the intensity scale after its registration of a photographic plate (traced out on the blackening scale) changes in such a way that the distance between points of equal intensity remains strictly unchanged. This characteristic of the law of the transformation of the curve into another enables the relative intensity of a point on the contour of a line registered on the blackening scale to be calculated directly using (2) without having to reconvert from the blackening scale to the intensity scale for the curve as a whole.

In the first of these methods of analysis mentioned above the use of the blackening curve is excluded completely, since the width of a standard line at a height equal to the blackening of the line of the test element (used for calculations of the relative intensity of both lines) does not depend on the form of the curve $S = S(I)$.

In the second method, on the other hand the regular change in intensity along the contour of the line together with the invariance mentioned above of the distance between points of equal intensity relative to transformation from the blackening scale to the intensity scale, is used for constructing the characteristic curve of the emulsion, by means of which the analysis is subsequently carried out.

The values which are used as the original series of intensities in the method described for constructing the blackening curve are those which correspond to individual points on the contour of the X-ray spectral lines which are related to each other by the dispersion law. When the true profile of a line is registered on an X-ray plate it will be transformed into another profile because of the non-linear relation between blackening and intensity. The law which governs this transformation can be found experimentally, if the property mentioned above is used viz., that on transforming one curve into the other, two symmetrical points on their contour (corresponding to one value of blackening of intensity) remain equidistant. In this way, having measured the width of the line at any cross-section of the experimental profile (on the blackening scale), relation (2) can be used and the value of I/I_0 corresponding to a given blackening value on the true profile of the line (on the intensity scale) found.

The use of formula (2) presumes a knowledge of Γ[1]. In the absence of deformations of the profile of the line brought about by the spectrogram itself, this quantity is an atomic constant equal to the sum of the widths of the initial and final levels for an electron transfer in the emmitting atom. When working with a focussing spectrograph with a bent crystal the value of Γ differs to varying extents from the natural width of the spectral line and should be considered as a constant which is dependent on the characteristics of the apparatus used. The difference between this quantity and the true value of $_{true}$ is particularly great when working with a Johann type of spectrograph where $(\Gamma - \Gamma_{true})$ depends on the cotangent of the angle of reflection and in some cases can exceed the natural width of the line by 2-3 times. It is essential that all this be borne in mind when attempting to use these types of apparatus for carrying out sensitive physical invest-

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[1] The case where the values of Γ for two lines being compared are equal is an exception. In this case having measured the width of the two lines at an arbitrary but identical cross section of the two lines, it is possible to calculate the relative intensity, not knowing Γ by using the relation $\frac{I_1}{I_2} = \frac{\left(\frac{x_1}{x_2}\right)^2 + (k-1)}{k}$

where k is a quantity which depends on n_2, and has a value which is practically constant at $\sim 1.12 \pm 0.02$ for $8 < n_2 < 11$.

igations. When working with an analytical method (in the case where the form of the lines registered does not undergo assymetrical distortions) it is important only to indicate a reliable method for the experimental determination of Γ, in which the latter is considered to be related to the apparatus constant and numerically equal to the width of a line at half the intensity of its maximum.

If during an analysis it is possible to use the $K\alpha_1$ line of any element as the standard, then finding is a simple elementary problem. Since the ratio of the intensities of the $K\alpha_1$ and $K\alpha_2$ lines of all elements are equal to or very nearly 0.5 (i.e., $n = 2$) then it follows from formula (2) that the value of Γ for the $K\alpha_1$ line for any form of the relation $S = S(I)$ and for any absolute value of the blackening of the $K\alpha_1$ line should be equal to its width measured at the peak height of the $K\alpha_2$ line of the element.

Similarily the width of the $L\alpha_1$ line measured at the height of the peak of the $L\alpha_{2,1}$ line should amount to 2.85 Γ [1]. In the general case (e.g., when using a singlet line as the standard line) the half width of the line Γ can be determined by two methods. According to the first method, a part of the line is artificially weakened by means of aluminum foil of a known density. Having subsequently measured the width of the unweakened part of the line at the peak height of the blackening of its weakened part, Γ is calculated by formula (2). In practice the second method is particularly suitable, in this method side by side with the test line, the $K\alpha_{1,2}$ doublet of another element (the standard) is photographed. The amount of the standard element in the specially prepared mixture is chosen so that the blackening of the $K\alpha_1$ line on the X-ray spectrogram is equal to or near to the blackening of the test line.

Under these conditions the half width of this line Γ can be determined directly by measuring the width at the height of maximum blackening of the $K\alpha_2$ line of the standard element.

It was shown experimentally that the basis of this analytical method described is fundamentally sound. In a series of tests the conclusions concerning the dispersion form of the X-Ray $K\alpha_{1,2}$ lines of elements with atomic numbers greater than or equal to 30 were again confirmed, and the constancy of the value of Γ as measured by one of the methods described above proved for a wide range of blackening of the lines and a wide range of spectrogram backgrounds. A consideration of the experimental results enables us to affirm that despite a ten-fold change in blackening of the lines and background of the spectrogram the values of Γ characterizing each of the emission lines considered, remain constant with a mean error of 3%. Similarily the width of the $L\alpha_1$ line measured at the peak height of the $L\alpha_2$ line remains constant. The half width calculated by means of these measurements is in good agreement with the value obtained by direct calculation of the profile of the curves for true intensities.

In order that the results may be more general and independent of the thickness and the degree of uniformity of the photographic emulsion it is expedient to use one-layer films.

Since the change in width of the precision slit of the photometer within the limits 0.2 - 0.5 mm does not (as control test showed) affect the results, it is better to give them preference over wider slits; their use ensures that the photometric results are practically independent of the irregularity of the distribution of the emulsion grains of the photographic film. We used a slit width of 0.4 mm for an increase of 20 times in the photometer.

When working with focussing X-ray spectrographs the accuracy and reliability of quantitative X-ray spectral analysis which is based on measurements of the form

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[1] It is assumed that the ratio of the intensities of the lines is equal to 0.11.

and width of the X-Ray spectral lines, to a large extent depends on the constancy of these parameters along its length. It has been shown that during the bending of the crystal in the spectrograph by means of a method proposed by Vainshtein, Narbutt and Gilvarg [15], the width of the line at the focus of the apparatus remains practically constant along several tens of millimeters of its length. Apparently similarily close results can be obtained when using another of the methods proposed for bending crystals in X-ray spectrographs [16, 17, 18] or by its simplest modification [19].

In contrast to this the application of the widely used crystal holders of an old type of construction does not allow the width of the line and the intensity of the line to be kept constant for a sufficiently large part of the line as a result of the imperfect bending of the crystals in them. The value of r, e.g., characterizing the width of the line in this case can change sometimes by as much as 50% for a displacement of 30-40 mm along the line. Therefore when constructing calibration curves or carrying out analysis, a definite part of the line chosen once and for all should be used all the time. With this aim in view, measurements of the width of the line should always be carried out at the point along its length where its maximum intensity is observed.

When such a method of measurement is adopted then the accuracy is not affected even by the notorious effect of "spectrum creep", which is known to be connected with an insufficient stability of the position of the focal point of the X-ray tube of the spectrograph and usually causes the X-ray spectroscopist a lot of trouble. The possible error in choosing the position of the point at which the width is measured does not in this case exceed 1 mm, while the error in measuring the width of the line which is related to the error of choosing the position of the point is considerably lower than the statistical error of the measurement.

As the practical use of this new analytical method of getting stable results showed, it is essential to take into account yet another possible source of error in measuring the width of the spectral lines. The width of the lines, just like the relative intensity for different wave lengths[1], depends on the angle of rotation of the anticathode surface of the spectrograph tube in relation to the horizontal surface - α. For this reason the size of this angle would be definitely fixed when carrying out an analysis. According to our experimental results, the optimum value of α should be near to 25°.

The quantitative X-ray spectrographic methods of analysis considered were used for developing special analytical methods suitable for the quantitative determination of heavy elements.

The samples analyzed contained groups of elements to be determined simultaneously in amounts from 1 - 15%, the relative content in the samples varying from 1 : 10 and vice versa. Despite such wide variations in the contents of the elements in the samples, corresponding to variations in the blackening of the lines of 7 - 10 times [2], the percentage content of the standard element in them can be left unchanged. The amount of the standard element in the test is usually chosen so that the blackening of the $K_{\alpha 2}$ line of the standard element during the exposure time necessary for performing an analysis, lies within the range of S = 0.3 to S = 0.7. Under these conditions, as special experiments showed, the analytical results obtained by both methods are in good agreement with each other; their mean

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1) This phenomenon is explained fundamentally by the difference in the values of the absorption for the two lines in the surface layer of the anode on which the test sample is placed.

2) It is well known that in the analytical methods used hitherto, blackening of the lines should not differ by more than 2 - 2.5 times in order to avoid large errors.

accuracy is not less than 6 - 10% of the actual content of each of the elements which are being determined simultaneously. For some concentrations and for favorable ratios of the amounts of the standard elements in the test mixtures the accuracy of their determination by the method described increases. This increase in accuracy is connected with the fact that the magnitude of the error in measurement calculated e.g., for the first of the methods considered, according to the formula

$$\Delta = \frac{2\left(\frac{\Gamma}{x}\right)^2 \frac{dx}{x}}{\left[1+\left(\frac{\Gamma}{x}\right)^2\right]^2}, \qquad (3)$$

changes regularly with the ratio of the intensities compared, I/I_0, and attains a maximum value in the region where this ratio has its mean values. From equation (3) it also follows incidentally that for Γ/x = const the error in measurement is less, the greater x, i.e., the wider the profile of the standard line used by the investigator.

This conclusion is in good agreement with experimental observations.

Methods of Analysis Based on the use of the Transformed Characteristic Curve of the Emulsion

The P-Transformation and its Properties. In the previous paragraph consideration was given to one of the methods whereby during X-Ray spectrographic analysis, it is possible to overcome difficulties connected with the non-linear characteristic curve of the emulsion of the photographic material used. The second approach capable of leading to an improvement in the methods of X-Ray spectrographic analysis is an examination of the possibilities of "rectifying" the characteristic curve used for analysis.

Despite the fact that both these approaches to the problem are directed to the same end, have many points in common, and by the correct use of the results obtained from each method are capable of essentially supplementing each other, each approach has its own independent significance and requires special consideration. This is more expedient, in contrast to that which was true in considering the first group of analytical methods; in the last case the X-ray spectroscopist has the possibility of relying on the experience and some actual results obtained by workers in optics [20, 21, 22] who have for a long time been using (in addition to) the blackening $S = \log i_0/i$, the value of $W = \log(i_0/i - 1)$ which in a number of cases enables (in the coordinates $W - \log I$) the "latitude of the emulsion" of the photographic material to be increased at the expense of the underexposure region. Here as usual i_0 and i are the values of the galvanometer kicks, which correspond to the places on the photographic plate not subjected to the action of light, and the blackened places respectively.

In general it is natural to pose the question of looking for, and using a sufficiently simple transformation for carrying out X-Ray spectrographic investigations whereby a well defined comparison can be made of such values of some function P, as would lie fairly accurately on the straight line (4) with the values of S for a wide blackening range (e.g., from $S = 0.1$ to $S = 2$).

$$P = \gamma_P \log I - i_P \qquad (4)$$

where γ_P and i_P are constants, while I is the intensity of the monochromatic X-Ray radiation registered by means of a photographic film. Bearing in mind that in virtue of what was said above the function P for certain special values of the coefficients determining its form, should agree with W and that the curve relating W to $\log I$ in the underexposure region (in which differences in the values of W and S become important) bends towards the side opposite to the characteristic curve

$\underline{S} = \underline{S}(\log I)$, it is natural to propose that in the first approximation the function which answers condition (4) can be represented in the form $\underline{P} = \underline{W} + \underline{l}(\underline{S} - \underline{W})$, where $\underline{l}$ is a constant which is characteristic of the chosen type of emulsion.

In order to construct and use the P-transformation in practice it is necessary to have some information on two of its characteristic functions $\underline{l}$ and γ_P. Information on the third constant i_p is not essential for the solution of the majority of analytical problems. The coefficient $\underline{l}$ can be determined by several methods. The first of these methods, which is completely analogous to the method used in optics [22], assumes a knowledge of the characteristic curve of the emulsion $\underline{S} = \underline{S}(I)$ for the type of photographic materials used. According to this method two intervals differing in size $\Delta \log I$ are chosen on the abscissa of the blackening curve; one in the underexposed region, the other on the straight line part of the curve. Within the limits of each of the intervals chosen, the values of the increase in blackening ΔS and the values of ΔW corresponding to them are determined. Further using the fact that according to (4) $\Delta P_1 = \Delta P_2$ the value of $\underline{l}$ is calculated by the formula

$$\underline{l} = \frac{\Delta W_2 - \Delta W_1}{\Delta S_1 - \Delta S_2 + (\Delta W_2 - \Delta W_1)} \qquad (5)$$

It is more convenient to use the second method in those cases where the blackening curve is not known. In this case in order to calculate the required constant of the $\underline{P}$ transformation it is possible to use the fact that the ratio of the intensities of the $K\alpha_{1,2}$ doublet components of the elements is constant. A constant interval, approximately 0.3, corresponds to this ratio on the abscissa of the characteristic curve of the emulsion. Therefore, the $K\alpha_{1,2}$ lines of an element are registered on the test film twice so that the blackening of each of the lines in the doublet in one case exceeds $S = 0.8$ (the limit of the normal blackening region for X-Rays) and in the other case is less. Having made the corresponding measurements it is not difficult then to calculate the value of the requisite parameter of the transformation by means of a formula analogous to (5). Simultaneously on the basis of the results of the same group of measurements the coefficient of contrast of the emulsion can also be determined, γ_S.

Similarily for the determination of $\underline{l}$ a method can be used which is based on the artificial weakening of one of the spectral lines by means of an absorber of known density. This method, however, in the majority of cases is not so convenient as that described above.

If the blackening curve is known then a knowledge of the transformation parameter $\underline{l}$ enables the curve $P = P(\log I)$ to be drawn and the second of the quantities γ_P of interest to the analyst to be determined experimentally. If the characteristic curve is not known then the value of γ_P can be calculated by means of the relation

$$\gamma_P = \gamma_S \left[\underline{l} + (1 - \underline{l}) \frac{d\overline{W}}{dS} \right] \qquad (6)$$

where $d\overline{W}/dS = 10^{\overline{S - W}}$ is the mean value of the product dW/dS within the limits of the straight line part of the blackening curve. It is possible to show that for the films normally used in X-Ray spectrography $d\overline{W}/dS$ should be very nearly 1.08.

We shall now consider the results of an experimental study of the properties of the P-transformation in the X-Ray part of the spectrum.

Several types of film were studied including: aerofilm, negative type "A" film, positive type "nitro 1" film, and the X-Ray films "XX", and "Agfa". The effect of various developers was studied in which the degree of contrast and the capacity of giving fine grain development differed. The purpose of these experiments was to verify the correctness of the fundamental relations appertaining to

the transformation considered in the X-Ray part of the spectrum, and a study of the relation between the parameters of this transformation and the wave length of the rays registered on the film. It is only after doing this that it is expedient to consider some general questions of procedure connected with the use of the P-transformation in investigating X-Ray emission spectra.

In all the experiments described a blackening curve was constructed by the application of a method [14] which is based on using the law of change in intensity along the contour of the X-Ray spectral lines.

A group of curves which is typical of our experiments is shown in Figs. 1 and 2. The curves in Fig. 1 represent respectively the blackening curve, and its corresponding curve relating the function P and log I obtained with an X-Ray film of the "XX" type using a normal developer in a wave length region of ca. 1400 XU. Fig. 2 shows the same curve for a shorter wave length part of the spectrum (λ = 700 - 800 XU). An example of the method of calculating the transformed characteristic curve is represented in Table 1.

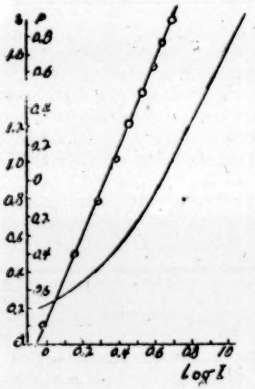

Fig. 1

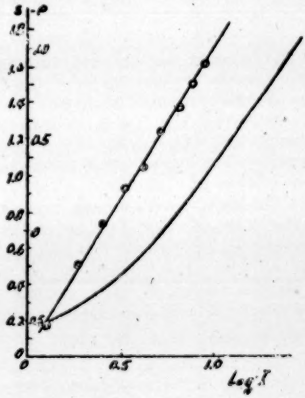

Fig. 2

TABLE 1

S	W	S − W	−0.65 (S − W)	Y
0.1	−0.587	+0.687	−0.446	−1.033
0.2	−0.233	0.433	−0.282	−0.515
0.3	−0.002	0.302	−0.196	−0.198
0.4	+0.180	0.220	−0.143	+0.037
0.5	+0.335	0.165	−0.107	+0.228
0.6	+0.474	0.126	−0.082	+0.392
0.7	+0.603	0.097	−0.063	+0.540
0.8	+0.725	0.075	−0.049	+0.676
0.9	+0.842	0.058	−0.038	+0.804
1.0	+0.952	0.046	−0.030	+0.922

It is evident that in both cases the characteristic curve of the emulsion can be equally well "rectified" in the region for S = 0.1 to blackening values which

are equal to or even exceed S = 2 by means of the P-transformation. In the part of the spectrum considered there is a regular change in both the coefficient of contrast of the film and in the absolute value of the coeffieient $\underline{1}$ which has a negative sign, with decreasing wave length of the X-Rays. In this part therefore the values of the second constant which are near in magnitude usually correspond to near values of the first of these constants. Thus the relation between these values can be represented by the smooth curve depicted in Fig. 3. Here, the values of the coefficient of contrast of the film are plotted along the abscissa while the corresponding mean values of $\underline{1}$[1] are plotted along the ordinate.

The relation between the coefficient of contrast and the wave length in the part of the spectrum considered is represented graphically in Fig. 4. It is noteworthy that alongside the almost complete constancy of this value in one region of the spectrum, in another part a regular change is observed which is sufficient to introduce appreciable distortions into the results of quantitative X-Ray spectrographic analysis in those cases where it is not specially taken into account by the analyst.

In parallel with these experiments the changes in value of γ_S with the type of photographic material used were studied. As the experiments carried out under completely identical developing conditions showed, the changes within the limit of the film of a definite type are insignificant. At the same time on switching from one type of film to another the value of γ_S changes appreciably.

Thus, for the films which we studied, the value of the maximum coefficient of contrast for X-Rays for a wave length of ca 1500 XU was a minumum (γ_S = 1.5) for negative highly sensitive emulsions. For the special types of emulsion used in aerial photography and also the X-Ray films of type "Agfa" and "positive nitro-1" the value of γ_S remained practically constant at 2.5. Films of the "XX" type were characterized by an intermediate value of γ_S = 2. It was shown in a series of comparative tests that for films of different classes (e.g. "XX" and "Agfa") a similar type of relation exists between the values of the coefficient of contrast and wave length. The curves obtained were completely identical and were only displaced relative to each other from the ordinate.

Special consideration was given to verification of the validity of relation (6). The results obtained are adduced in Table 2. Here k_E and k_T are the exerimental and theoretical values of the coefficient of proportionality between γ_S and γ_P.

$$\eta = \frac{k_E}{k_T}$$

TABLE 2

Element	λ	γ_S	γ_P	$\underline{1}$	k_E	k_T	η
Cu	1537	2.06	2.50	−1.30	1.21	1.16	1.04
Zn	1432	1.96	2.36	−1.20	1.21	1.18	1.03
Ga	1337	1.80	2.06	−0.75	1.14	1.14	1.00
As	1177	1.60	1.90	−0.67	1.12	1.11	1.01
Y,Zr,Nb and Mo	870–700	1.45	1.67	−0.65	1.15	1.13	1.02

1) The value of $\underline{1}$ depends to a fairly large extent on the path of the blackening curve in the region of underexposure, where errors in the determination of the position of separate points of the characteristic curve increase for a variety of reasons. Therefore in order to calculate the coefficient in which we are interested it is expedient to take the mean of the results of a large number of parallel sensitometric experiments as a preliminary.

From a consideration of this table it can be stated that if the analyst does not have a blackening curve at his disposal, then relation (6) in which dW/dS can be assumed to be equal to 1.08 is completely suitable for calculating the value of

The accuracy with with which this parameter of the P-transformation can be calculated is not less than the accuracy of the sensitometric test itself.

In a special series of experiments a study was made of the effect of the conditions under which the X-Ray spectrograms were developed on the form of the transformation function. Experiments were made using the copper $K\alpha_{1,2}$ doublet. The spectral lines were registered on "Agfa" films. The time of development and the composition of the developer were both varied. Three types of developer were used (I) contrast; (II) normal, and (III) fine grain.

An examination of the experimental results obtained leads to the conclusion that the maximum coefficient of contrast which can be obtained by means of a selected type of emulsion changes very little with the composition of the developer. For the three types of developer mentioned above the respective values of the maximum coefficient of contrast were 3.2;3; and 2.9. One of the curves relating γ_S to the development time obtained with a normal developer is shown in Fig. 5. The developers are distinguished only by the rate of development and the intensity of the fog developed on the spectrogram. On the other hand a change in the composition of the developer or in the developing conditions which often lead to an appreciable change in the form of the characteristic curve of the emulsion in the region of underexposure, or to a displacement of the limits of its straight line part, appreciably affect the value and even the sign of the basic parameter of the P-transformation, viz., the coefficient l. When this happens, however, no direct connection can be observed between the composition of the developer, the rate with which it acts or the degree of "contrast", and the change in value of the transformation parameter. Thus in our experiments there is practically no difference in the value of this constant for the developers I and III, which differ most from each other in their properties. On the other hand the value of this constant for I and III differs essentially from the value of the constant characterizing the P-transformation when using Developer II. The value of γ_P as was to be expected changes with changes in l so that in each case it can be calculated by relation (6).

2. Use of the P-Transformation for X-Ray Spectrographic analysis. The use of the P-transformation enables many of the questions which the analyst is constantly coming up against in carrying out quantitative X-Ray spectral analysis to be solved more simply and with greater precision than has been possible hitherto. Despite the limited framework of the present article we shall consider some of these questions in particular.

a) The Calculation of the Continuous Background of X-Ray Spectrograms and its Application as an Internal Standard for Quantitative X-Ray Spectrographic Analysis. The characteristic lines of the X-Ray spectra which are used for carrying out quantitative spectral analysis are always located on a more or less intense continuous background. Calculation and elimination of the background present an important and not always easily soluble problem. Various investigators often use for this purpose different and not always sufficiently precise methods. In those cases where the background of the X-Ray spectrograms appears uniform, it is sometimes completely ignored by analysts who depart from the view that as a consequence of the curvelinearity of the characteristic curve of the emulsion, the effect of a background of the same value on the blackening of lines of different intensities must be different.

The P-transformation, by means of which it has already been shown the characteristic curves used for analysis can be "rectified", enables this problem to be

solved easily and accurately[1]. Let the value $\underline{1}$, determining the form of the P-transformation, be known for a given type of emulsion and for given developing conditions. Then a knowledge of this constant enables the mutual relation between the blackening S of the film and the value of the function $\underline{P}$, satisfying condition (4) to be found. Experimentally only the change in blackening of the line at its maximum S_{L+B} and the blackening of the background S_B of the spectrogram at a definite distance from the line are measured.

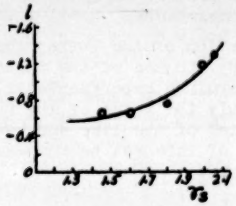

Fig. 3

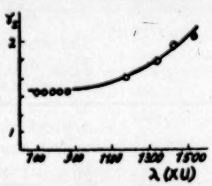

Fig. 4

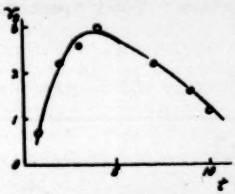

Fig. 5

Calculating the background of the spectrogram means finding the blackening S_L on the basis of a knowledge of the quantities measured experimentally, S_L being the blackening of the line if there were no background at all. A P-transformation is realized. In order to do this the values of P_{L+B} and P_B corresponding to the blackenings S_{L+B} and S_B respectively are calculated.

In accordance with the postulated problem we shall look for P_L in the form

$$P_L = P_{L+B} - \gamma_P D, \tag{7}$$

where D is a correction appertaining to the determination.

Having substituted in formula (7) the values of P from formula (4) and carrying out the necessary simplifications we get

$$D = \log I_{L+B} - \log I_L \tag{8}$$

which is equivalent to the equation

$$D = \log \frac{I_{L+B}}{I_B} - \log \frac{I_L}{I_B} . \tag{9}$$

Assuming that $I_{L+B} = I_L + I_B$ and putting $I_{L+B}/I_B = k$, it is possible to transform (9) into its final form

$$D = \log k - \log (k - 1), \tag{10}$$

in which according to formula (4)

$$\log k = \frac{P_{L+B} - P_B}{\gamma_P} \tag{11}$$

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[1] This was considered in optical spectroscopy in 1942 [21].

It is particularly convenient to use the relation between D and k if it is represented in the form given in the table (vide e.g. [23]).

Thus a knowledge of P_{L+B}, P_B and γ_P enables one to calculate precisely the effect of the continuous background, to calculate the value of P_L according to (7), and if necessary to find the blackening S_L corresponding to this value of the P-function. In this connection therefore the difficulties which crop up during attempts to use the background of X-Ray spectrograms as an internal standard for carrying out quantitative X-Ray spectrographic analysis[1] are easily surmountable.

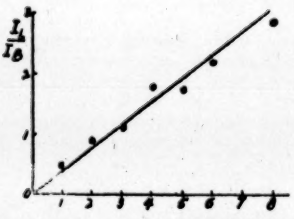

Fig. 6

The application of the P-transformation enables us by the use of the values of P_{L+B} and P_B determined experimentally, to calculate directly the value of the ratio of the intensities of the line and background which is of interest to the analyst using the fact that

$$\frac{I_L}{I_B} = \frac{I_{L+B} - I_B}{I_B} = k - 1 ,$$

where k is the root of equation (11).

As our experiments have shown (vide e.g., Fig. 6) this method, which is distinguished by its simplicity and by a number of other advantages, can be successfully used immediately for semi-quantitative determination of elements in objects of a complex composition with the normal order of accuracy for such determinations, ca. 20% of the actual value.

There is no doubt that after the introduction into X-ray spectrographic laboratory practice of new high voltage equipment, whereby the operating conditions of the X-Ray tube of the spectrograph can be maintained at a high level of stability, this method will enable analyses to be carried out with much greater accuracy. This is connected with the fact that the different degree of the relation between intensity of the line and background and the voltage makes the accuracy of the method described dependent to a greater extent than that of other methods, on the stability of the high tension applied to the X-Ray tube.

b) A Quantitative X-Ray Spectrographic Method of Analysis. The use of the P-transformation enables one to simplify and essentially improve the X-Ray spectrographic method of analysis. By means of it one simple, uniform, scheme of analysis, the limits of which are sufficiently wide, can be planned instead of the many special analytical methods in use at present. Let us consider the question in its most general form. Let the values of P_L' and P_L'' be known, they correspond to the two lines compared by the analysis carried out. The wave lengths of these two lines differ essentially from each other[2]. In general, this means that the coefficients of the P-transformation γ_P and i_P for the lines with the wave lengths considered are different, therefore

$$P_L' = \gamma_P \log I_L' - i_P' \quad \text{while} \quad P_L'' = \gamma_P'' \log I_L'' - i_P'' .$$

If we consider the difference $P_L' - P_L''$. It will obviously be equal to

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1) This method which was proposed as long ago as 1942 [24] is at present winning its rightful place in optical spectroscopy.

2) Both P_L' and P_L'' are reduced to a null background by means of the method, described in the previous paragraph.

$$P'_L - P''_L = \gamma'_P \log I'_L - \gamma''_P \log I''_L + i''_P - i'_P$$

Let $\gamma''_P = \gamma_P \pm \delta$, then

$$P'_L - P''_L = \gamma'_P \log \frac{I'_L}{I''_L} \pm \delta \log I''_L + (i''_P - i'_P),$$

from which

$$\frac{P'_L - P''_L}{\gamma'_P} = \log \frac{I'_L}{I''_L} + \frac{i''_P - i'_P \pm \delta \log I''_L}{\gamma'_P}.$$

Assuming as usual that $I = kc$, where c is the atomic percentage of the element in the test, we get the equation

$$\frac{P'_L - P''_L}{\gamma'_P} = \log \frac{c'}{c''} + \left[\frac{i''_P - i'_P}{\gamma'_P} + \log \frac{k'}{k''} \pm \frac{\delta}{\gamma'_P} \log I''_L \right], \qquad (12)$$

where since $\delta \geq \gamma_P$, the expression in brackets can, to a first approximation be considered as a constant which is characteristic of the pair of lines chosen, and of a given type of emulsion.

Equation (12) written in the form

$$\frac{P'_L - P''_L}{\gamma'_P} = \log \frac{c'}{c''} + a, \qquad (13)$$

should be verified in a wide content range of the test element. Experimental tests confirm the correctness of this conclusion. One of the curves obtained during these tests is given in Fig. 7. The constant can be determined from the condition that for $P'_L = P''_L$, $a = \log \frac{c''}{c'}$. In some special cases however it is practically zero. This naturally simplifies the development and carrying out of the analysis.

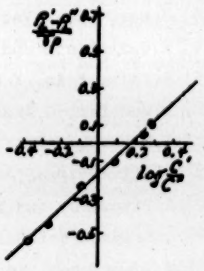

Fig. 7

SUMMARY

1. Results are given of a comparative study of two new methods of X-Ray spectrographic analysis which are based on the use of the form of the spectral lines. It has been shown that if a number of conditions are observed both the analytical methods considered lead to results which are in good agreement. The mean accuracy of the analysis is 6 – 10% of the actual content of an element and increases in certain concentration ranges.

2. The possibility of "rectifying" the characteristic curve of the photographic emulsion by means of the P-transformation has been demonstrated, and the properties of this transformation have been studied in the X-Ray part of the spectrum. A relation between the basic parameters of this transformation and the wave length of the light and the developing conditions respectively has been demonstrated.

Possible ways of using this P-transformation for carrying out quantitative X-Rsy spectrographic analysis have been indicated.

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THE APPLICATION OF THE ION-EXCHANGE CHROMATOGRAPHIC METHOD IN THE ANALYSIS OF COPPER-IRON CERAMIC ALLOYS AND BRONZES

D.I.Ryabchikov and V.E.Bukhtiarov

Tsvet's chromatographic method [1] in all its forms: adsorption, precipitation, distribution, and ion-exchange chromatography, has found more and wider applications in analytical chemistry in recent years.

Ion-exchange chromatography has been applied sucessfully for the analysis of cations. This method cannot be regarded as an independent method in analytical chemistry, but it represents an exceedingly important intermediate stage in the analysis of complex materials.

By means of ion-exchange it is possible to separate the components of a mixture in a pure state and subsequently to determine the nature and amount of each of them by normal chemical or physico-chemical methods.

Ion-exchage chromatography can be applied in chemical analysis, e.g., for concentrating salts which are found in dilute natural mineral solution or in industrial wastes before subsequent determination of their total concentration or the concentration of individual components of the mixutre. Of vital importance in analytical procedure is the removal of ions which interfere with the determination of certain elements. This removal can be effected by the use of ion-exchange columns e.g. the separation of iron and aluminum ions from any sulfuric or phosphoric acids present in solution. A prospect with the greatest possibilities for analytical chemistry is the separation of certain cations from mixtures of them by transforming them into anionic forms on the basis of their amphoteric character or by complex formation. It is also possible to separate elements of similar properties by using "cationite" (cation-exchange resins) columns in conjunction with complex compounds of the components of the mixture being analyzed which are of different stabilities. Further enumeration will not exhaust the possible applications of ion-exchange chromatography in chemical analysis.

Natural ion-exchange compounds, both organic (substances rich in humic acids - peat, brown coal,) and inorganic (aluminosilicates) have been widely used in practice for a comparatively long time. But the application of ion-exchange resins increased considerably after the production of synthetic inorganic ion-exchange materials (permutites) and particularly after the preparation of synthetic organic resins capable of exchange-ionites.

All the synthetic exchange resins known at the present can be divided into two groups. To the first group belong those resins with acid properties and which are capable of exchanging cations-cationites. They are polymerization or condensation products of phenol or styrene, and their derivatives with formaldehyde. As a result of special treatment the active acid groups $-SO_3H$; $-CH_2SO_3H$; $-COOH$; phenol groups $-OH$ etc., enter into their composition. Because the active groups are structurally linked with the resin skeleton they cannot go into solution. Only the hydrogen ions of these groups ($R-SO_3H$) or cations which have substituted hydrogen remain mobile.

The second group is comprised of resins possessing basic properties and capable of exchanging anions-anionites. The ion-exchange properties of these anionites are determined by the presence of amine or imine groups in them.

The exchange and regeneration processes of ion-exchange resins can be described by the equations for the following reactions

$$\text{Cationites} \quad nRH + Me^{n+} = R_nMe + nH^+ \quad \text{(exchange)}$$

$$R_nMe + nH^+ = nRH + Me^{n+} \quad \text{(regeneration)}$$

where $Me = Na^+, K^+, Mg^{2+}, Al^{3+}, Fe^{3+}$, etc.

$$\text{Anionites} \quad nROH + An^{n-} = R_nAn + nOn^- \quad \text{(exchange)}$$

$$R_nAn + nOH^- = nROH + An^{n-} \quad \text{(regeneration)}$$

where $An = Cl^-, SO_4^{2-}, PO_4^{3-}$ etc..

The ion-exchange process can be considered as a heterogenous process between the active groups of the resin and the ions in solution, The reaction proceeds in accordance with the law of mass action.

Synthetic resins which are to be used as ion-exchange compounds must satisfy a number of requirements. Primarily they must be stable in different chemical media and possess high mechanical stability in the dry state and also particularly in the swollen state. The resins used for analytical purposes, while possessing a good absorptive capacity, should at the same time under the respective conditions give up the absorbed ions completely. These requirements are satisfied to a large extent by makes of resins where they are prepared in the form of small spheroids. Ionites prepared by breaking down hard masses of resin often have uneven grain surface and therefore as a rule they hold a part of the ions absorbed by them very firmly.

The comparative characteristics of some ion-exchange resins both of Russian and foreign manufacture were studied by Ryabchikov, Senyavin, and Filippova [2]. Of the Russian makes the most suitable for analysis are the cationites SBS, SDV-1 and SD-2 and the anionite MMG-1.

A large amount of work has been devoted to the application of ion-exchange resins in analytical chemistry. A detailed literature survey was given in the article of Ryabchikov and Teretev [3]. Several investigations have been made by Soviet analysts [4-6] on the separation of mixtures of metals in the course of their analytical determination.

In the present article some examples of the use of exchange-ion resins for the separation of individual metals in the analysis of alloys are considered.

Separation of Copper From Iron in the Analysis of Copper-Iron Ceramic Alloys

The normal method of separating copper and iron is based on the differences in their behavior with ammonia, but as a consequence of the adsorption of copper by the ferric hydroxide precipitate, precipitation has to be repeated several times. Even then the desired result is not always attained, and the analysis takes a long time. The application of cation-exchange columns radically improves the process of separating these metals

The fundamental idea of the chromatographic method consists in passing a solution through a layer of cationite in one definite direction; this is achieved by means of the simple apparatus shown in the diagram[1]) This method of normal filtration through a column of cationite is called frontal analysis. This method was used throughout the investigation.

1) See Plate, page 431.

The column was filled with the cationite SBS[1] in the hydrogen form.

The separation of copper and iron is possible if one of these elements, e.g., iron can be converted into a complex anion; in such a case, the copper in the form of its simple ion will be held by the cationite in the column as a result of the reaction:

$$2R\text{-}SO_3H + Cu^{2+} = (R\text{-}SO_3)_2Cu + 2H^+ ,$$

while iron, being in the form of an anion, will pass through into the filtrate.

Sodium pyrophosphate was chosen as the complexing agent. However it was shown that the sodium pyrophosphate, for nearly neutral solutions, reacts with both metals forming complex compounds according to the equations:

$$2Fe_2(SO_4)_3 + 6Na_4P_2O_7 = 2Na_6[Fe_2(P_2O_7)_3] + 6Na_2SO_4 ,$$

$$CuSO_4 + Na_4P_2O_7 = Na_2[CuP_2O_7] + Na_2SO_4 .$$

In practice at a pH of 7.5, as a result of complex formation between both the copper and iron salts and sodium pyrophosphate, both metals passed through into the filtrate on passing a solution of the mixture through a cationite column.

The situation can be basically altered if the pH of the original solution is adjusted to pH 10-11 (by addition of ammonia). In this case the pyrophosphate complex of iron remains unchanged because of its high stability. The pyrophosphate complex of copper, being less stable, changes in ammoniacal media according to the reaction:

$$Na_2[CuP_2O_7] + 4NH_4OH + Na_2SO_4 = [Cu(NH_3)_4]SO_4 + Na_4P_2O_7 + 4H_2O .$$

The copper becomes a part of the cation in the complex formed.

Thus by the successive treatment of the solution, being analyzed with pyrophosphate and ammonia, the two metals become parts of different ions; iron becomes part of the anion $[Fe_2(P_2O_7)_3]^{6-}$, while copper becomes part of the cation $[Cu(NH_3)_4]^{2+}$.

On passing the test solution through a column of cationite, the iron passes through into the filtrate while the copper is retained on the column combined with the active group of the resin. The separation of copper and iron and their subsequent determination were carried out as follows;

1 g of alloy was dissolved in 30 ml 30% HNO_3 and 20 ml 10% H_2SO_4 with heating until white fumes of sulfuric acid appeared. The salts obtained were dissolved and the solution made up to 250 ml in a standard flask. For each determination 50 ml of solution was taken; to this aliquot was added a saturated solution of sodium pyrophosphate until the simple pyrophosphates originally formed dissolved again. To the solution of complex pyrophosphates thus obtained was added 25 ml of concentrated ammonia and after careful mixing the solution was filtered through a cationite column in which the resin was in the hydrogen form, at the rate of 4 ml/minute. The residue in the beaker and the iron from the column were washed with 3% ammonia solution. 10% KCNS was used to test that all the iron had been removed from the column. 50 ml of 20% NaOH was added to the filtrate containing iron and the solution heated until it clarified. The precipitate of ferric hydroxide formed was then filtered and dissolved in 20% hot hydrochloric acid; the solution was transferred to a 250 ml standard flask and made up to volume. The iron was then determined in an aliquot by means of permanganate.

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[1] This cation was prepared at the Plastics Division of the D.I.Mendeleev Chemico-Technological Institute, Moscow

The copper was stripped from the column by eluting with 20% HCl to start with, and then with 10% HCl. That all the copper had been removed was checked by the absence of a blue color when 5 drops of the eluent from the column was added to a solution of potassium iodide and starch. 15 ml of concentrated H_2SO_4 was added to the filtrate containing copper, after which the filtrate was evaporated till white fumes of sulfuric acid appeared. The salts obtained were dissolved in 100 ml of water and the copper determined iodometrically.

Results for the determination of copper and iron in copper-iron ceramic alloys using SBS are given in Table 1.

These results show that satisfactory agreement with those obtained by another method.

Tartrates and citrates were also tested as potential complexing agents. However these salts formed such stable complexes with iron that the metal could not be removed completely from the filtrate even with concentrated alkalis.

TABLE 1

No. of Expt.	Normal Method (in %)		By the use of cationite (in %)	
	Copper	Iron	Copper	Iron
1	59.64; 59.58; 59.56	39.60; 39.60; 40.01	59.56; 59.80; 59.64; 59 46; 59.56	39.74; 39.72; 39.74; 39.45; 39.45
2	49.78; 49 48; 49.72	49.82; 49,54; 49.66	49.76; 49 74; 49.80; 49 76; 49.80	49.54; 49.54; 49.53; 49.52; 49.52
3	29.82; 29 96; 30.00	68.54; 68,39; 68.72	29.84; 29 96; 30.00; 29 96	68.54; 68.71; 68.55; 68.54;

In parallel with the cationite SBS we used the American product "Dowex 50". Although Dowex 50 has a greater absorptive capacity than SBS, we did not get such good results with it.

Separation of Copper From Aluminum in the Analysis of Bronzes

Bronzes of marks BrA5, BrA7 and BrA10 have copper as the basic component with additions of from 4-11% aluminum.

The normal analytical method for these bronzes is based on either electrolytic separation of copper or its precipitation with thiosulfate and subsequent iodometric determination, while the aluminum is determined in the filtrate by means of 8-hydroxyquinoline. It follows from this that for the first method (electrolytic separation) mentioned, platinum electrodes, etc., are necessary, while the second method takes a long time to perform.

Copper can be readily separated from aluminum by using a cationite column. As in the previous instance one of the elements to be separated is converted by means of a complexing agent into a complex anion (aluminum) while the other remains as the cation (copper).

Tartaric acid in ammonia solution was chosen as the complexing agent. In the presence of these reagents, aluminum forms a tartrate complex in which it forms part of the anion $[Al_2(C_4H_2O_6)_3]^{6-}$ which is formed by the reaction

$$Al_2(SO_4)_3 + 3C_4H_6O_6 + 12NH_4OH = (NH_4)_6[Al_2(C_4H_2O_6)_3] + 3(NH_4)_2SO_4 + 12H_2O\ .$$

Copper under these conditions forms part of the cation – $[Cu(NH_3)_4]^{2+}$ which is itself formed according to the reaction

$$CuSO_4 + 4NH_4OH = [Cu(NH_3)_4]SO_4 + 4H_2O .$$

On passing a solution treated in this way through a cationite column, the aluminum passes through into the filtrate while the copper in the form of the complex cation is retained by the active groups of the resin according to the reaction:

$$2R\text{-}SO_3H + [Cu(NH_3)_4]^{2+} = (R\text{-}SO_3)_2Cu(NH_3)_4 + 2H^+ .$$

Copper and aluminum were separated by the following procedure;

0.25 g of bronze was dissolved by heating with 15 ml 30% HNO_3 and after addition of 10 ml 10% H_2SO_4 the solution was evaporated until white fumes of sulfuric acid ceased to be evolved. The salts obtained were then dissolved in 25 ml water and 2 g of tartaric acid added to the solution obtained; after this had dissolved 50 ml of concentrated ammonia was added. The solution was carefully mixed and then passed through a cationite column containing SBS in the hydrogen form. The aluminum was eluted from the column with 3% ammonia. To the filtrate obtained (ca. 400 ml) hydrochloric acid was added till a weakly acid solution was obtained, when it was evaporated to 200-250 ml. Aluminum was then precipitated from the evaporated solution, which had been made alkaline with ammonia, with 8-hydroxyquinoline. The aluminum hydroxyquinolate was finally dissolved in hydrochloric acid and the aluminum determined volumetrically by the bromate-bromide method.

The copper was removed from the cationite first with 20% and then with 10% hydrochloric acid solution. A solution of potassium iodide plus starch was used to check that all the copper had been removed. The filtrate containing the copper, after addition of 15 ml concentrated H_2SO_4, was evaporated until white fumes of sulfuric acid appeared. The salts were then dissolved in 100 ml of water and the copper determined iodometrically. Results for the determination of copper and aluminum in bronzes using SBS are given in Table 2.

TABLE 2

Type of Bronze	Normal method (in %)		By the use of cationite (in %)	
	Copper	Aluminum	Copper	Aluminum
BrA5	95.00	5.15	94.92; 94.72; 95.24	4.96; 5.12; 5.34
BrA7	92.42	7.49	92.00; 92.40; 92.40	7.58; 7.56; 7.68
BrA10	90.70	9.30	90.64; 90.52; 90.90	9.48; 9.44; 9.52

Separation of Copper, Aluminum, and Iron in the Analysis of Bronze

Bronze mark BrAFe 9-4 contains copper as the basic component, aluminum (from 8-10%) and iron (from 2-4%).

Bronze mark BrAFeMn 10-3-1.5, in addition to copper as the major component, also contains aluminum (9-11%), iron (2-4%) and manganese (1-2%). The normal chemical method of analysis is identical with that described above. After the electrolytic separation of copper, the aluminum is separated from the iron (manganese) by the usual method. The aluminum is finally determined by means of 8-hydroxyquinoline while the iron is determined by the permanganate method. Manganese is determined by the persulfate method on a separate aliquot.

The drawbacks of this method are the same as those mentioned above. The position can be radically improved if a cationite column is used for separating the

copper from aluminum and iron. As before the aluminum and iron are converted into complex anions by means of a complexing agent while the copper is absorbed by the resin as a cation.

In this rather more complicated case sodium pyrophosphate cannot be used as the complexing agent for iron, or tartaric acid for aluminum. Salicylic acid seemed to be a suitable complexing agent in this case. We established that at a pH of 10 in the presence of salicylic acid and ammonia iron and aluminum can be complexed as the anions $[Fe(Sal)_3]^{3-}$ and $[Al(Sal)_3]^{3-}$, while the copper remains in the form of the complex cation $[Cu(NH_3)_4]^{2+}$.

The [illegible] chemistry of the interaction of these metals with salicylic acid is treated in detail in the literature [7, 8].

However, because of the poor solubility of salicylic acid in water, we used sulfosalicylic acid instead. Sulfosalicylic acid is much more soluble, while it possesses complexing properties of the same order as salicylic acid.

It should be noted that if any manganese is present it will behave differently. Manganese forms a complex anion which is not stable enough so that a test solution containing manganese on passing through a column will take some of the manganese through into the filtrate with it, together with the iron and aluminum, while the rest of it is retained by the resin because of the decomposition of the complex by the active groups of the cationite.

Copper was separated from aluminum and iron and subsequently determined in production samples as follows:

0.25 g of alloy was dissolved as indicated above. The salts obtained were dissolved in 25 ml of water and 25 ml of a 20% solution of sulfosalicylic acid, and 25 ml of concentrated ammonia solution added. After the solution had been thoroughly mixed it was passed throught a cationite in its hydrogen form at the rate of 4 ml/minute. The column was eluted with 3% ammonia to remove any residues of aluminum and iron and the total volume of the filtrate made up to 400 ml. 30 ml of 20% sodium hydroxide was then added to the filtrate and heated till the solution clarified. Iron as ferric hydroxide was filtered off and determined by the permanganate method. The aluminum in solution as aluminate was acidified with hydrochloric acid. It was then precipitated from an ammoniacal solution with 8-hydroxyquinoline and determined by the bromide-bromate method. The copper was extracted from the column and determined iodometrically.

Results for the determination of copper, aluminum, and iron in the bronzes of these marks are given in Table 3.

TABLE 3

No. of sample	Normal method (in %)			By the use of cationite (in %)		
	Copper	Aluminum	Iron	Copper	Aluminum	Iron
Standard	88.05	9.80	1.97	88.00; 88.16; 88.12; 87.92	9.91; 9.72; 9.78; 9.84	1.90; 1.99; 1.99; 2.10
8	85.51	8.80	3.80	85.60; 85.30; 85.34; 85.38	8.78; 8.80; 8.80; 8.92	3.69; 3.80; 3.70; 3.76
9	81.56	10.76	7.27	81.80; 81.44; 81.60; 81.40	10.92; 10.80; 10.76; 11.00	7.20; 7.12; 6.96; 7.20
68a[1]	85.63	9.82	2.74	85.48; 85.80; 85.60; 85.64	10.08; 10.04; 10.02; 10.00	2.88; 2.64; 2.82; 2.76
2[1]	86.29	9.88	3.66	86.12; 86.48; 86.40; 86.32	9.75; 9.81; 9.86; 9.85	3.72; 3.43; 3.65; 3.67

1) There was 1.49-1.55% manganese in samples 68a and 2.

Separation of Manganese and Iron When Present Together

The chromatographic separation of this pari of metals is of interest in itself, apart from the analysis of bronzes and ceramic alloys.

Taking into account the chemical characteristics of manganese to be converted easily into the ionic state MnO_4^-, it seemed that the problem would be solved by simple oxidation of the test mixture whereby the iron would be converted into its trivalent form (Fe^{3+}). In practice however this did not work. On passing a solution containing manganese in the form of its anion through a cationite column, it was reduced as a result of the reducing properties of the resin, and in its reduced form, manganese just like iron was held back by the active groups of the resin. If the acidity was increased to any large extent, so that the manganese was retained in the septi-valent stage, then the iron also passed through into the filtrate with the manganese. It was shown that the best results were obtained when the mixture of iron and manganese was treated with a solution of ammonium oxalate at a pH of 5. Under these conditions the manganese remains as a positive bivalent ion (Mn^{2+}) while the iron becomes a part of a complex anion of the composition $[Fe(C_2O_4)_3]^{3-}$ according to the reaction:

$$FeCl_3 + 3(NH_4)_2C_2O_4 = (NH_4)_3[Fe(C_2O_4)_3] + 3NH_4Cl.$$

The oxalate complex of the iron remains stable in weakly acid solutions and is not destroyed on passing through a cationite column.

The procedure adopted was as follows:

To a neutral solution containing manganese and ferric sulfate was added 15 ml of 30% HNO_3 and 10 ml H_2SO_4, after which the solution was evaporated to white fumes of sulfuric acid. The salts obtained were dissolved in 25 ml water and 4% ammonium oxalate solution added until all the iron has been combined into a complex.

Concentrated ammonia was then added dropwise till the blue color of Congo red turned red. The solution thus prepared was passed through the column containing cationite in the hydrogen form at the rate of 4 ml/min. Any residual iron was eluted from the column with distilled water until a negative test was given with thiocyanate. The manganese was removed from the column with 10% H_2SO_4. The metals in the respective fractions were then determined by the usual methods. Results are given in Table 4.

TABLE 4

Mg taken		Mg found	
Iron	Manganese	Iron	Manganese
10.20	22.50	9.90; 10.00; 10.00	19.60; 19.90; 21.70
20.40	15.00	19.90; 19.40; 20.20	13.70; 14.60; 14.50
20.40	7.50	19.90; 19.60; 19.50	7.60; 7.00; 7.00
30.60	15.00	30.00; 29.90; 29.60	13.70; 13.20; 14.50

SUMMARY

1. Conditions have been selected [ionite (ion-exchange resin), size of column, filtration rate, complexing agents, and media] for the separation of the components of ceramic alloys and bronzes before their analysis.

2. Copper and iron can be separated by using sodium pyrophosphate in ammoniacal media as the complexing agent.

3. Copper and aluminum can be separated by using tartaric acid in ammoniacal media as the complexing agent.

4. Copper can be separated from aluminum and iron by using sulfosalicylic acid in the presence of excess ammonia as complexing agent.

5. Iron and manganese can be separated in the presence of ammonium oxalate at a pH of 5.

6. The methods developed enable copper to be determined in alloys without the use of platinum.

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ALEXEI MIKHAILOVICH VASILEV

(On his 70th birthday)

This year Professor Alexei Mikhailovich Vasilev celebrates his 70th birthday and also his 45th year of scientific and teaching activity. He is one of the oldest analytical chemists of our country - a Doctor of Chemical Sciences; he has been an active worker for science and technics in the RSFSR and TASSR.

Having finished at the Perm classical preparatory school Vasilev entered the Natural Sciences, Physico-Mathematical Faculty of Kazan University in 1902. He finished his course in 1907.

In 1908 he took his state examination and got a first class diploma. Prof. F.M.Flavitsky' proposed that he stay at the University in order to prepare for a Professorship. Within one year Vasilev passed his master's degree and became a lecturer and started taking courses in "Gas Analysis". In the autumn semester of 1912 he was entrusted with the important course on "Qualitative Analysis", while from 1913 onwards he also took the course on quantitative analysis.

A.M.Vasilev's scientific and teaching activities only reached their fullest development after the Great October Socialist Revolution. In 1918 he was appointed as professor in Kazan University. He put in a great deal of work and energy in organizing an independent chair of analytical chemistry in the University, he still heads this section. He deserves credit for creating an unified course in analytical chemistry, instead of descriptive and purely empirical courses of qualitative and quantitative analysis.

In 1930 a Chemical-Technological Institute was organized in Kazan. Vasilev became a professor at the Institute and headed the chair of analytical chemistry, as he still does at present. He contributed his wide teaching experience and knowledge to the development of a new industrial college. Vasilev is a dean of the technological faculty, and serves as deputy of the director on the scientific and educational side and sometimes fills the post of Director of the Institute.

Vasilev's scientific activity is distinguished by its variety. He has published more than 100 papers mainly on inorganic and analytical chemistry. The first of his papers on analytical chemistry relate to his earlier period of scientific activity ("The application of nitron in nitric acid analysis") 1910,and "Indirect analysis of the halide salts of antimony and tin".

Vasilev has proposed quite a number of analytical methods which have been adopted in various textbooks on analytical chemistry. Of these we may note "A rapid method for the simultaneous determination of calcium and magnesium",published in 1932 in "Factory Laboratories".

This method has considerable advantages in speed and is no less accurate than other similar methods.

A.M.Vasilev also worked on volumetric gas analysis. His work on volumetric gas analysis for the determination of potassium by means of cobaltinitrite,published in 1930,is of the greatest practical significance. This method consists in the decomposition of potassium cobaltinitrite with ferrous salts to give nitric oxide.

One of the fundamental branches of his scientific activities in analytical chemistry was the study of the phenomenon of coprecipitation. Under his guidance a large amount of work was devoted to the study of the precipitation of many practically insoluble salts in the presence of various cations and anions. The precipitate of barium sulfate in the presence of trivalent iron, thorium, nitrates, chlorides, bromides, borates and the precipitates of lead sulfate, calcium oxalate and many others were studied.

It was therefore natural and not accidental that Vasilev has developed an interest in recent years in chromatography, and in particular in the study of ion exchange processes which are gaining such importance in analytical chemistry.

Vasilev's work on the washing of precipitates is worthy of attention. He proposed an original method of washing precipitates with a saturated solution of the precipitant. This method of washing was tested on various precipitates ($SrSO_4$ etc.), and took its place in several textbooks as recommended.

Of Vasilev's theoretical work in analytical chemistry his proposed formula for the extent of neutralization should be mentioned (Proc. Kazan Chem.-Tech. Inst. No.2,1934).

This formula gives the relation between the degree of titration of a weak acid and its dissociation constant for any given hydrogen ion concentration.

This formula with the usual degree of accuracy enables one to make interesting conclusions for volumetric analysis; it is possible to determine the extent of titration of acid with various indicators; to calculate the hydrogen ion concentration in solutions of the acid salts of dibasic acids;and to calculate the amount of acid which must be neutralized in order to get a buffered solution with a given pH.

While acknowledging the importance of physico-chemical methods of analysis, he does not forget the classical methods and continues to develop them in his work. He considers the application of organic reagents in analytical chemistry of great significance and writes excellent reviews on this question which are published in the "Proc. of the Commission on Analytical chemistry".

In recent years Vasilev has turned his attention to the study of ion-exchange and the application of this technique in analysis.

His scientific activities are not confined within the walls of the University laboratories. Numerous factory laboratories in the Tatar Republic consult him on a wide range of subjects.

He plays an active part in the work of the Kazan scientific societies. He has been a member for a large number of years of the committee of the Kazan branch of the D.I.Mendeleev All-Union Chemical Society, and is one of the oldest members of the Society of Naturalists in Kazan University

With his wide knowledge and penetrating understanding of a large number of chemical problems he has written more than 50 references for scientific workers in Kazan and other cities of the Soviet Union trying for their doctor's or candidate's degree.

Vasilev's work on methods is well known. He has published a number of articles on methods of teaching analytical chemistry and has read reports on this subject at conferences. His "Collection of problems in analytical chemistry" is a valuable text book for teachers and students.

His fruitful scientific teaching and social activities have gained him acknowledgement and high rewards from the Soviet Government.

In 1940 in connection with the 10th anniversary of the Kazan Chem. Tech.

Institute and the 50th anniversary of industrial education in Kazan, the Praesidium of the Supreme Soviet of TASSR assigned to Vasilev the honorable title of Meritorious Worker in Science and Technology of the TASSR.

In 1947 he was given the same title of the RSFSR.

He was awarded the order of the Red Banner of Labor and a medal "For Valiant Service in the Patriotic war 1941-1945."

On his birthday his friends and a wide circle of Soviet Analytical chemists send him their sincerest wishes for good health, new strength and long life, and a continuation of his fruitful work for the glory and prosperity of Soviet chemistry and for the good of our beloved country.

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CRITICISM

A NEW AND USEFUL BOOK

N.P.Komar "A Collection of Problems, Exercises, and Questions in Qualitative Analysis". Published by Kharkov State University, Kharkov, 1952, pp. 1-230. Circulation 5000. Price 5 roubles 90 kopecks.

Despite the variety of subjects dealt with in Russian chemical literature, the publication of N.P.Komar's book fills a definite gap, because no other book has yet been devoted to qualitative analysis in which there is such a complete and penetrating exposition of the mathematical side of the chemical processes studied in qualitative analysis. Although many books have been devoted to calculations in physical chemistry and chemical thermodynamics (R.Abeg and O.Sakhur 1924; D. Noakes 1934; R.Venner 1950 etc.) and these questions are also dealt with in various textbooks on thermodynamics (A.F.Kapustinsky, 1936; J.Partington and A.V. Rakovsky, 1932; M.Kh.Karapetyants, 1949) only "Problems in Quantitative Analysis", by A.P.Musakun, A.I.Khrapovsky, S.P.Shaikind and S.M.Efrov (State Chem. Press 1950) containing the simplest calculations on quantitative determinations, and A.M.Vasilev's "Collection of problems in analytical chemistry" can be mentioned which deal with analytical chemistry. Vasilev's book is somewhat closer in content to Komar's book, but the problems in the former are simple while the system of ionic equilibrium is not considered in such detail or from so many aspects as in Komar's book.

N.G.Glinka's ("Problems and Exercises in General Chemistry", 1947), which is most like the book under review, concerns general chemistry and is designed for less advanced students.

Komar's book, which is new in concept and new by reason of its complete grasp of the whole range of questions discussed, contains fresh, new, and interesting material which has been carefully thought and worked out.

It consists of four sections.

I. Construction of equations.

II. Problems on the theory of ionic equilibria.

III. Questions and problems for oral examinations in a course on qualitative analysis.

IV. Solutions of typical problems.

The section dealing with problems in the theory of ionic equilibrium is very interesting. It deals with the calculation of the degrees of dissociation from cryoscopic data, and from electroconductivity results; calculations of equilibrium in solutions of weak acids and bases, in solutions of weak acids and their salts, and of acid salts; equilibria in systems containing two weak acids; equilibria in solutions of multibasic acids; equilibria in systems containing indicators; and equilibria in systems containing complex ions. Many problems are devoted to hydrolysis, to the calculation of the solubility product by solubility and vice versa. Calculations are made of the minimum concentrations required for the formation of precipitates; a few cases are considered of equilibrium connected with the solution of difficultly soluble compounds; equilibria connected with the solution of amphoteric hydroxides; equilibria during complex formation; equilibria in systems with oxidizing or reducing agents; and the determination of optimum concentrations of precipitant.

This list shows how wide and all embracing is the treatment given to the theory of ionic equilibrium which lies at the basis of almost all qualitative reactions in analytical chemistry.

Considerable attention is given to complex formation, beginning with the terminology, compilation of equations,and calculations of the process of complex formation. Among the tables of constants at the end of the book, Table 6 contains constants for a very large number (35) of complex ions; thus this important section is treated very thoroughly.

Oxidation – reduction processes are not treated quite so fully.

Thus problems (No. 619-638) basically reduce to dissolving metals and sulfides in acids, while very few problems of the type of No. 638,on the oxidation of the manganous ion to permanganate by lead dioxide in sulfuric acid,are given. There are however a large number of such problems in analytical chemistry,e.g.,the reduction of ferric chloride with stannous chloride, the solution of manganese dioxide in acid solutions of ferrous sulfate, etc. etc..

A table of the constants of oxidation – reduction processes is given at the end of the book (in detail on 8 pages); it would however have been more convenient to give a table of oxidation – reduction potentialswhich chemists are accustomed to use, in particular in volumetric and electrometric methods of analysis.

The main virtue of this book is its freshness and the variety of examples chosen by the author. Together with important analytical reactions and in addition to the usual elements dealt with, cesium, rubidium, and thallium often figure in the examples; problems in which methylamine crops up introduce variety into the material, since methylamine does not often turn up in such problems. True there are some defects in the consideration of elements of the 6th group; only one or two questions are devoted to selenium and tellurium, while tungsten and uranium are not included at all, although there are quite a few problems relating to these elements which could have been considered. This however does not affect the complete and all round exposition of the processes considered in this book.

The mathematical side of this book is particularly worth dwelling on. In addition to calculations which can be solved by direct substitution of the respective numerical data in the equations of physical-chemistry, the majority of the problems require considerably more complex calculation. These calculations could present a lot of difficulties to many chemists, if the solution of such problems were not adduced, and the principles used in solving them enunciated. Thanks to this the reader can pick up the methods for solving similar calculations, not only those in the book but those which crop up for similar reactions in practical analytical work.

There is no doubt that this book will be a very great help to a large number of chemists, will enable them to improve their qualifications and scientific education, and will enlarge their knowledge of chemical processes on the quantitative side. In addition it will serve as an stimulus for starting new investigations on the quantitative evaluation of processes.

The publication of this book is a valuable contribution to Soviet chemical literature.

V.V.Shcherbina

The Ultramicro Method of Chemical Analysis, p. 377.

Fig. 5. Apparatus for carrying out ultramicro chemical determinations.

Fig. 6. Precipitate of silicic acid in an evaporated solution

Spectrophotometry in Chemical Analysis. p. 385.

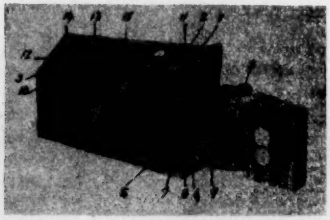
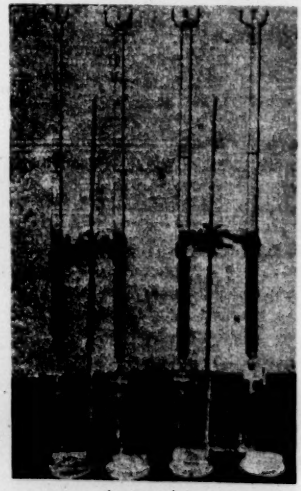


Fig. 3. External appearance of the SF-11 spectrophotometer.
1,2) Handle and scale for the monochromator slit; 3) wave length set up; 8) cell compartment; 9) cell set up in front of the slit; 11) connection for the photoelectric part; 12) regulator for the dark current of the photoelement; 13) wave length scale; 15) handle of the reading potentiometer.

Application of the Ion-Exchange Chromatographic Method in the Analysis of Copper-Iron Ceramic Alloys and Bronzes. p. 417



Apparatus